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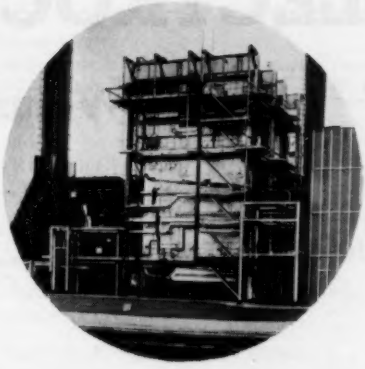

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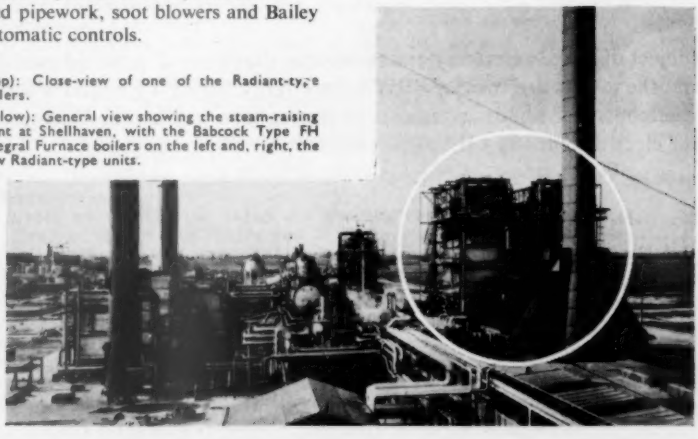
(Top): Close-view of one of the Radiant-type boilers.

(Below): General view showing the steam-raising plant at Shellhaven, with the Babcock Type FH Integral Furnace boilers on the left and, right, the new Radiant-type units.



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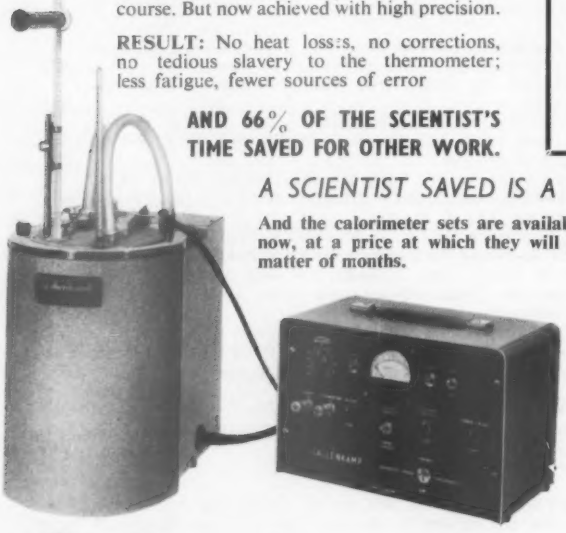

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*The Kinetics of the Sorption of Methanol on Cellulose**

P. FUGASSI and G. OSTAPCHENKO

The sorption of gaseous methanol on cellulose has been studied at 30, 35 and 45°C. The process follows a rate equation which is second order relative to the number of unoccupied sorption sites and has an activation energy of 5700 cal/mole. A mechanism for the sorption process is suggested involving adsorption of methanol on the surface followed by permeation of the solid by methanol molecules. The kinetic data require that the surface adsorption be of the multilayer type. From the kinetic data a new sorption equilibrium isotherm is derived which fits the experimental equilibrium data over the entire pressure range studied, from a relative pressure of 0·1 to a relative pressure of 0·9. From this equation and from data for the adsorption of tertiary butyl alcohol on cellulose it is shown that most of the methanol is held by internal sites in the cellulose.

FOR the sorption of methanol on coal, it was found[1] that the moles of methanol taken up at time t at some constant pressure and at constant temperature were given by the equation

$$W = k_x W_e^2 t/(1 + k_x W_e t) \quad \ldots . [1]$$

In equation 1, W is moles of methanol held by one gramme of coal at time t, k_x is the experimental velocity constant, and W_e is the maximum weight of alcohol (moles) held by one gramme of coal at the given temperature and pressure. The experimental velocity constant, k_x, was found to be independent of the pressure over a considerable range of pressure and hence is a true velocity constant in the sense that it is a function of the temperature only.

Limited data in the literature appeared to show that the same equation was valid for the sorption of polar gases on swelling gels such as cellulose. As cellulose is considered one of the precursors of coal it was thought desirable to investigate the kinetics of methanol sorption on cellulose in detail.

EXPERIMENTAL

Apparatus

The sorption of methanol on cellulose was measured gravimetrically, using a McBain–Bakr type adsorption balance. The spring was made of Ni-Span C wire and had a sensitivity of 1·57 mg/mm extension. Spring lengths were measured by a cathetometer to 0·1 mm. The sample, in the form of fibres, was carried in a glass bucket weighing about 200 mg. Sample weights were about 300 mg. The apparatus consisted of the balance, a 2 l. flask to add sufficient volume to the system so that during sorption experiments the methanol pressure did not vary by more than 1 mm of mercury, a mercury manometer, and a storage flask for the methanol. Mercury-sealed stopcocks were used

* Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, New York Meeting, September 1957.

throughout. The pumping system was a two-stage mercury diffusion pump backed by a mechanical pump. The entire apparatus was housed in an air thermostat whose temperature could be held at $\pm$ 0·1°C.

Chemicals

Absolute methanol, Mallinckrodt A.R., was used as received. It was stored over Drierite. Tertiary butyl alcohol was redistilled. The sample of cellulose was prepared for us by the Hercules Powder Co. Cotton linters were washed with caustic soda solution, bleached with chlorine and then washed with distilled water. No further treatment of the material was made except that before the start of kinetic experiments a cellulose sample, after evacuation to constant weight, was allowed to remain in contact with methanol vapour for several days. The sorption of methanol on cellulose is isothermally reversible; evacuation of the system always caused the cellulose to return to a weight practically identical with the starting weight.

Procedure

After evacuation of the system until the cellulose sample showed constant weight, methanol vapour was admitted to the system and readings of the spring length taken at various times. The spring lengths were converted into weights making no correction for buoyancy which can be shown to be negligible or for adsorption of methanol on the glass bucket and spring. Experiments using an empty bucket showed that methanol adsorption on the glass bucket and the metal spring could be neglected up to relative pressures as high as 0·9. The fundamental data, then, are weights at known time intervals including the equilibrium weights characteristic of each pressure.

CALCULATION OF VELOCITY CONSTANTS

From the experimental data, a value of the fraction of the reaction, f, could be calculated for each value of the time. f is defined as $(W_t - W_0)/(W_e - W_0)$ where W_0 is the sample weight at time, $t = 0$, W_t is the weight at $t = t$, and W_e is the equilibrium weight at time $t = \infty$. All weights are expressed as moles. The value of $f/(1 - f)$ was plotted against the time giving straight lines through the origin. The slope of this straight line is $k_x W_e$ and since W_e is measured for each pressure and temperature k_x can be calculated. In general, points fell on a straight line and the line passed through the origin. A sample rate plot is shown in the upper portion of *Figure 1*. In all experiments readings were taken until at least 80 per cent of the equilibrium sorption was attained. At low relative pressures, $c = 0{\cdot}1$, experimental points corresponding to the initial stages of the reaction were above the straight line. This behaviour will be discussed later.

Sorption of a vapour by a solid is necessarily an exothermic process. If the rate of heat evolution is greater than the rate of heat removal by the thermostat then the sample will not be at thermostat temperature. Some evidence is needed to show that such temperature effects are not large for the given system. The rate equation previously given can be rearranged into the form,

$$t/W = A + Bt \qquad \ldots . [2]$$

In this equation t and W have their usual significance and A, B are constants. Plots of t/W versus t will permit evaluation of A and B. Inspection of the equation shows that B must be $1/W_e$. If now the kinetic data used in the upper half plot of *Figure 1* are plotted as is shown in the lower half of *Figure 1*, a value of W_e can be obtained which might be termed the kinetic value of W_e.

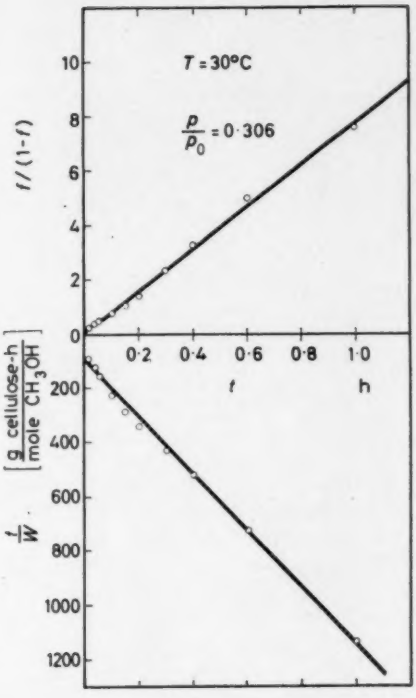

Figure 1. Plots for the velocity constant (upper) and the kinetic value of W_e (lower)

W_e can also be measured at equilibrium where transient temperature effects are absent. If the kinetic value of W_e agrees within one per cent with the equilibrium value of W_e as it does for the experimental data described here, then it can be concluded that for the sorption of methanol by cellulose, the expected temperature effect is not causing serious error. For the experiment plotted in *Figure 1*, the kinetic value of W_e is $10{\cdot}0 \times 10^{-4}$ in comparison with the equilibrium value of W_e of $9{\cdot}95 \times 10^{-4}$. The units of both values of W_e are moles methanol per gramme of cellulose.

EXPERIMENTAL DATA

The experimental values of k_x and W_e are tabulated in *Table 1*. It will be noted that the value of the experimental velocity constant passes through a maximum as the relative pressure, c, decreases.

Since a true velocity constant, k, must be a function of temperature only,

the experimental velocity constant, k_x, must be equal to k multiplied by some function of the relative pressure, c. Separation of k from k_x requires that a mechanism of the process be formulated. Even such an operation does not ensure that k is actually known because both velocity constants and equilibrium constants have a similar dependence on temperature. In other words, independent equilibrium data are needed to make sure that the term k is really not k multiplied by an equilibrium constant.

Table 1. Experimental values, k_x and W_e

T °C	c	k_x*	W_e†	T °C	c	k_x*	W_e†
30	0·894	5·8	22·6	35	0·268	13·0	8·8
30	0·700	16·3	18·1	35	0·119	1·9	5·1
30	0·500	19·2	13·6	45	0·863	9·3	21·2
30	0·306	7·9	10·0	45	0·697	26·7	16·9
30	0·125	2·5	5·3	45	0·491	31·0	13·1
35	0·848	16·4	21·1	45	0·294	13·1	8·8
35	0·669	21·4	17·3	45	0·088	1·9	4·5
35	0·486	29·0	12·9				

* Units of k_x are [g cellulose/moles methanol × h] × 10^{-3}.
† Units of W_e are [moles methanol/g cellulose] × 10^{-4}.

It will be necessary to anticipate the discussion of the mechanism for the sorption process to be given later. It is postulated in brief that the mechanism of the sorption process is a two-step process. The first step, known experimentally and theoretically to be rapid, is the adsorption of methanol molecules on the surface of the cellulose. The second step, which determines the reaction rate as the slower step, is the migration of methanol from the surface into the interior. From this type of mechanism it is necessary that in the simplest case

$$k_x = k\theta \qquad \ldots . [3]$$

where k_x is the experimental velocity constant, k is the true velocity constant and θ is the fraction of the surface sites covered.

Now the surface adsorption of methanol on cellulose can be of two types: monomolecular with one methanol molecule on one site or polymolecular with more than one methanol molecule on one site. For monomolecular adsorption, the Langmuir adsorption isotherm holds and it can be shown that θ increases as c increases for all values of c. Since k_x goes through a maximum, θ likewise must go through a maximum as c increases. Consequently the surface adsorption of methanol on cellulose cannot be monomolecular. For polymolecular adsorption, the only alternative, the the surface adsorption at a given temperature will be shown to be given by the equation

$$\theta_n = \frac{(K_2)^{n-1} K_1 (cp^0)^n (1 - K_2 p^0 c)}{1 + K_1 p^0 c - K_2 p^0 c} \qquad \ldots . [4]$$

In equation 4 θ_n is the fraction of surface sites covered by n molecules and K_1, K_2 are equilibrium constants whose significance will be discussed later. c is the relative pressure and p^0, the vapour pressure of methanol at the temperature in question. The product, cp^0, is the pressure of methanol vapour actually present. Insertion of values of one, two, or three for n gives θ_1, θ_2, θ_3, the fraction of surface sites covered by one, two, or three molecules. It will be noted that the expression for θ_n contains two parameters, K_1 and K_2. From three kinetic experiments at different values of c but at the same temperature, k, K_1 and K_2 can be evaluated in turn for θ_1, θ_2, θ_3.

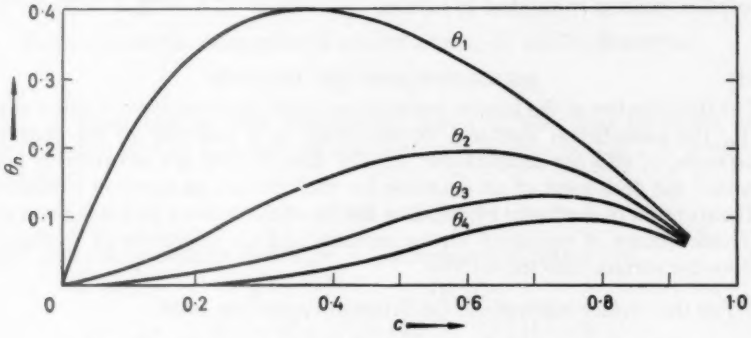

Figure 2. Variation of θ_n as a function of relative pressure, c, at 30°C

In *Figure 2* is shown a plot of θ_n as a function of c for $n = 1, 2, 3, 4$. The changing values of θ_n with increasing c are caused by the increase in the fraction of sites corresponding to higher values of n. It was found that the experimental values of k_x used in the equation, $k_x = k\theta_2$, gave the best fit of the experimental data. *Figure 3* is a plot of $k\theta_2$ against c. The points are the experimental points. The solid line is the calculated line using $8{\cdot}1 \times 10^4$ as the value of k (k_{true}) at 30°C.

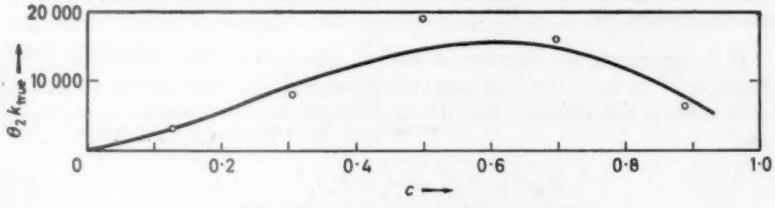

Figure 3. Variation of $k\theta_2$ with c

The values of K_2p^0 evaluated at three temperatures are 1·07, 1·03 and 1·05. These values of K_2p^0 are sufficiently close to unity that these kinetic data are experimental evidence for the correctness of the assumption, $K_2p^0 = 1$.

With this assumption, the equation for θ_2 can be simplified into

$$\theta_2 = K_1c^2p^0(1 - c)/\{1 + (K_1p^0 - 1)c\} \quad \ldots . [5]$$

From equation 5 and from the equation, $k_x = k\theta_2$, the values of K_1 and k can be obtained. However, the values of K_1 can also be obtained from the equilibrium isotherm and as the equilibrium measurements have the higher precision, it seems desirable to use these values in calculating k. The values of K_1p^0, as evaluated from the equilibrium isotherm at 30, 35 and 45°C are 3·0, 3·6 and 4·2 respectively. The corresponding average values of k in units of [g cellulose/moles methanol × h] for the three temperatures are: at 30°C, $8{\cdot}1 \times 10^4$; at 35°C, 10×10^4; and at 45°C, $12{\cdot}7 \times 10^4$. These values substituted in the Arrhenius equation give 5 700 cal/mole as the average energy of activation. This low value for the energy of activation is evidence that the sorption process is physical in nature.

EQUILIBRIUM SORPTION ISOTHERM

The full solution of the kinetic problem in closed equation form requires that W_e, the equilibrium sorption, be expressed as a function of the relative pressure, c, and the temperature, T. The kinetic data are informative and permit the derivation of an equation for the equilibrium sorption isotherm. The sorption of methanol by cellulose can be visualized as a two-step process: (*1*) adsorption of methanol on the surface, and (*2*) migration of methanol from the surface into the interior.

For the surface adsorption, the following equations hold:

$$G + S \rightleftarrows G \cdot S \quad \ldots\ldots [6]$$

$$G + G \cdot S \rightleftarrows G_2 \cdot S \quad \ldots\ldots [7]$$

$$G + G_2 \cdot S \rightleftarrows G_3 \cdot S \quad \ldots\ldots [8]$$

$$G + G_{n-1} \cdot S \rightleftarrows G_n \cdot S \quad \ldots\ldots [9]$$

In these equations G represents the gas molecule; S the surface sites; G • S, the surface sites holding one gas molecule; G_2 • S, the surface sites holding two gas molecules, etc.

If θ_1 represents the fraction of surface sites holding one molecule; θ_2 the fraction of surface sites holding two molecules; θ_n, the fraction of surface sites holding n molecules; then the equilibrium constants would be expressed as

$$K_1p^0 = \theta_1/(1 - \theta_1 - \theta_2 \ldots\ldots - \theta_n)c \quad \ldots\ldots [10]$$

$$K_2p^0 = \theta_2/\theta_1 c \quad \ldots\ldots [11]$$

$$K_np^0 = \theta_n/\theta_{n-1}c \quad \ldots\ldots [12]$$

where p^0 is the vapour pressure of the liquid and c is the relative pressure.

Further manipulation of these equations requires some simplifying assumptions connecting the equilibrium constants. If it is assumed that

$K_1 > K_2$ and $K_2 = K_3 = K_n$, two assumptions similar to the ones made in the derivation of the BET equation[2], then it can be shown that

$$\theta_1 = K_1 p^0 c\,(1 - K_2 p^0 c)/\{1 + (K_1 - K_2)p^0 c\} \quad \ldots . [13]$$

$$\theta_2 = K_2 p^0 c\,\theta_1 \quad \ldots . [14]$$

$$\theta_n = (K_2 p^0 c)^{n-1}\,\theta_1 \quad \ldots . [15]$$

These equations were applied to the kinetic data and it was shown that the kinetic data make two facts obvious: (*1*) the adsorption of methanol on cellulose involves more than one molecule for one surface site, and (*2*) $K_2 p^0 = K_3 p^0 = K_n p^0 = 1{\cdot}0$.

To determine the adsorption isotherm a term, Σ, will be defined as

$$\Sigma = \theta_1 + 2\theta_2 + 3\theta_3 \ldots . + n\theta_n \quad \ldots . [16]$$

Σ is a concentration unit representing moles of adsorbed molecules for $6{\cdot}02 \times 10^{23}$ sites or one mole of sites. It has been shown[2] that Σ is given by equation

$$\Sigma = \theta_1/(1 - K_2 p^0 c)^2 \quad \ldots . [17]$$

and using the condition that $K_2 p^0 = 1$ this equation reduces to

$$\Sigma = \frac{\theta_1}{(1-c)^2} = \frac{K_1 p^0 c}{[1 + (K_1 p^0 - 1)c]\,[1 - c]} \quad \ldots . [18]$$

which is essentially the BET equation, for multiplying Σ by a constant representing moles of sites for one gramme of solid gives W_e, the equilibrium adsorption in moles per gramme.

The second stage of the sorption process involves the migration of molecules adsorbed on the surface into the interior. This reaction can be represented by the equation

$$CH_3OH_{(surface)} + D \rightleftarrows D \cdot CH_3OH \quad \ldots . [19]$$

In this equation D represents interior sites. Calling ϕ the fraction of D sites holding methanol molecules, the equilibrium constant, K, for the above reaction can be written as

$$K = \phi/(1 - \phi)\Sigma \quad \ldots . [20]$$

and solution of this equation for ϕ gives

$$\phi = K\Sigma/(1 + K\Sigma) \quad \ldots . [21]$$

and the amount of sorption, W_e, is given by the equation

$$W_e = AK\Sigma/(1 + K\Sigma) \quad \ldots . [22]$$

where A is moles of interior sites for one gramme of solid. In setting up the last equation it has been assumed that the measured equilibrium sorption is the sorption on interior sites or, in other words, the surface adsorption contributes very little to the total sorption. An experimental and theoretical justification of this assumption will be given later.

It should be pointed out that the particular equation for W_e is not the general form. The reaction involving sorption on internal sites might be

$$n\,CH_3OH_{(surface)} + m\,D \rightleftarrows D_m \cdot (CH_3OH)_n \qquad \ldots . [23]$$

In all cases examined to date, $n = m = 1$. Furthermore it has been assumed by using $1 - \phi$ for the concentration of empty internal sites that the number of sites is independent of the amount of sorption. If sorption leads to the formation of new sites, by expansion of the gel, then the concentration of empty internal sites would be of the form, $1 - \phi + f(\phi)$. To date, no definite experimental evidence has been found which requires the use of a site-expansion term.

The sorption isotherm derived here, which is given by equations 22 and 18, yields an equation involving three parameters, A, K, K_1. It has been found to fit the equilibrium data in the literature for the sorption of polar gases by swelling gels. The extension of this equation to other systems will be the subject of a subsequent paper. But it can be stated that in general it will fit many systems up to relative pressures of 0·9 or greater.

The equation fits the equilibrium data for methanol sorption on cellulose also to 0·9. Application of the equation to the methanol–cellulose system gives the constants listed in *Table 2*.

Table 2. Constants for methanol sorption on cellulose

T °C	K_1 atm^{-1}	K	A
30	14·51	0·75	$2{\cdot}61 \times 10^{-3}$ *moles D sites/gramme*
35	13·60	0·65	$2{\cdot}65 \times 10^{-3}$ *moles D sites/gramme*
45	9·91	0·58	$2{\cdot}64 \times 10^{-3}$ *moles D sites/gramme*

The values of K in *Table 2* are dimensionless because Σ, used in K, represents a dimensionless quantity, the average number of adsorbed molecules held by one surface site. It will be noted that A is independent of the temperature as would be expected. K_1 and K vary in the normal manner with the temperature. Using the equation, $\Delta F^0 = -RT\ln K$, and evaluating ΔH from a plot of $\ln K$ against the reciprocal of the absolute temperature ΔF^0, ΔH and ΔS for surface adsorption (K_1) and for interior sorption (K) can be evaluated. These quantities have been tabulated in *Table 3*.

Thermodynamic data derived from measurements over limited temperature ranges would be expected to have low precision so that conclusions drawn from such data cannot be too definite. The heat of condensation of methanol vapour in the temperature range from 30° to 45°C is known to vary but assuming a constant value over this temperature range the heat of condensation is approximately − 8600 cal/mole. The fact that the value of ΔH for the interior sorption (D sites) differs greatly from the heat of condensation indicates that the interior sorption cannot consist of a large number of methanol molecules clustered near one site. In general, clustering of methanol

molecules so that interaction of methanol molecules with methanol molecules takes place should lead to higher values of the heat of reaction for the interior sorption than those observed.

Table 3. Thermodynamic values

Equilibrium	*T* °C	ΔF° *cal/mole*	ΔH *cal/mole*	ΔS *cal/°C*
Surface K_1	30	−1610	−5080	−11·5
	35	−1600	−5080	−11·3
	45	−1450	−5080	−11·4
Interior K	30	530	−1830	−7·8
	35	600	−1830	−7·9
	45	660	−1830	−7·8

REACTION MECHANISM

The following reaction mechanism is suggested for the kinetics of methanol sorption on cellulose:

$$G + S \rightleftarrows G \cdot S \quad \ldots\ [24]$$

$$G + G \cdot S \rightleftarrows G_2 \cdot S \quad \ldots\ [25]$$

$$G_2 \cdot S + 2D \rightarrow 2(D \cdot \tfrac{1}{2}G) + G \cdot S \quad \ldots\ [26]$$

$$G \cdot S + 2(D \cdot \tfrac{1}{2}G) \rightarrow G_2 \cdot S + 2D \quad \ldots\ [27]$$

$$G_2 \cdot S + 2(D \cdot \tfrac{1}{2}G) \rightleftarrows 2D \cdot G + G \cdot S \quad \ldots\ [28]$$

Reactions 24 and 25 represent the adsorption of the gas on S (surface) sites. Obviously additional reactions leading to the formation of species like $G_3 \cdot S$, $G_4 \cdot S$ are also involved but are not necessary for explanation of the kinetic data. All reactions involving surface adsorption of the physical type are known to be rapid both on theoretical and experimental grounds. The double arrow is used to indicate that these reactions are in equilibrium.

Reaction 26 is the slow rate-determining reaction for the sorption process. A molecule from a site of the $G_2 \cdot S$ type migrates into the interior and is held on two D (internal) sites. Two internal sites are required to explain the second order kinetics found experimentally. The nature of these sites will be discussed later. Reaction 27 is the reverse of reaction 26 and is necessary to account for the reversibility of the sorption process. Reaction 28 is a rapid equilibrium type reaction. It is postulated to have one G molecule held on one D site, which is indicated to be so from the previously derived sorption isotherm. Reaction 26 might be assumed to be the one involved in the swelling of the cellulose. Subsequent reactions of the same type such as reaction 28 are probably more rapid because they involve less swelling of the cellulose.

Using W to be $W_t - W_0$ or the increase in weight (moles) at time, t, and W_e to be $W_\infty - W_0$ or the increase in weight (moles) at infinite time, the differential equation for the process is

$$dW/dt = k_3\theta_2(W_e - W)^2 - k_4\theta_1(W)^2 \quad \ldots . [29]$$

Since f, the fraction of reaction, is W/W_e, this equation can be arranged to give

$$df/dt = k_3\theta_2 W_e(1 - f)^2 - k_4\theta_1 W_e f^2 \quad \ldots . [30]$$

Let B denote the term $k_4\theta_1/k_3\theta_2$. Introduction of B gives

$$df/dt = k_3\theta_2 W_e[(1 - f)^2 - Bf^2] \quad \ldots . [31]$$

which on integration and substitution of limits gives

$$k_3\theta_2 W_e t = \frac{1}{2B^{\frac{1}{2}}} \ln \frac{1 - f(1 - B^{\frac{1}{2}})}{1 - f(1 + B^{\frac{1}{2}})} \quad \ldots . [32]$$

Unfortunately, this equation is difficult to handle numerically because of the appearance of B in the logarithmic term. However, the experimental data indicate that, at higher pressures corresponding to higher values of c, B becomes smaller since θ_1/θ_2 is $1/c$. If B can approach a small number then the differential equation can be simplified to

$$df/dt = k_3\theta_2 W_e(1 - f)^2 \quad \ldots . [33]$$

which on integration and substitution of limits gives

$$k_3\theta_2 W_e t = f/(1 - f) \quad \ldots . [34]$$

Equation 34 was used for the calculation of rate constants setting $k_3\theta_2 = k_x$. The experimental work indicates that at low pressures ($c = 0{\cdot}1$) the full equation should be used. For single experiments it has been shown that the experimental data fit the full equation using the trial and error method for the evaluation of B. However, the low pressure region from $c = 0$ to $c = 0{\cdot}1$ is the region for which the experimental precision of the apparatus is low. This is the reason for limiting the experimental work to the region, $c > 0{\cdot}1$.

It will be noted that the data suggest only $G_2 \cdot S$ species on the surface furnish G molecules for the interior sites. The question naturally asked is why other types of surface species such as $G \cdot S$ and $G_3 \cdot S$ are not involved in the reaction. For the $G \cdot S$ configuration it appears that the G molecule is held more firmly on the S (surface) site than on the D (internal) site. The standard free energy differences at 30° C for the reactions

$$G + S \rightleftarrows G \cdot S \quad \ldots . [35]$$

and

$$G + D \rightleftarrows G \cdot D \quad \ldots . [36]$$

are about $-$ 1 600 and $-$ 450 cal/mole, or a difference of 1 150 cal/mole. Two reasons can be advanced for the relatively small participation of $G_3 \cdot S$, $G_4 \cdot S$ species in the adsorption reaction. In the first place the fractions of surface, θ_1, θ_2, occupied by each type are related by the equation

$$\theta_1 : \theta_2 : \theta_3 : \theta_4 = 1 : c : c^2 : c^3 \quad \ldots . [37]$$

and except at high values of c, the relative concentrations of $G_3 \cdot S$ and higher species are low (see *Figure 2*). In the second place the adsorption sites on polymeric materials need not, as with metals, be restricted to areas essentially equal to the area occupied by an atom. The area of the surface sites on cellulose could be much larger than the area of a single atom. Such sites could be visualized, for methanol adsorption on cellulose, as cooperative and hence adjacent functional groups such as hydroxyl. If this is true then the orientation of the surface units is of importance and the different types of sites correspond to adsorption on a heterogeneous surface. It is very probable that gaseous methanol molecules cannot penetrate the crystalline lattice of cellulose and where such a lattice is present on the surface, adsorption on such crystalline sites will not lead directly to sorption on the interior sites.

The reversibility of the sorption process is obviously dependent on the relative values of θ_1, and θ_2, which in turn depend on the pressure. If, in the system at equilibrium, the pressure of methanol is decreased θ_2 approaches zero faster than θ_1, and the reverse reaction predominates.

DESORPTION EXPERIMENTS

The rates of desorption of methanol from cellulose have been measured in a number of experiments but with the experimental conditions used here the data are not significant and have not been reported. The desorption data follow the same rate equation as the sorption data. This can be shown by plotting t/W against t. The slope of the straight line should be $1/W_e$. In desorption experiments all data fit on such a line. However, the experimental slope is always lower than $1/W_e$, where W_e has been determined from equilibrium measurements. Desorption experiments are made under a high vacuum and as desorption is an endothermic process it is believed that in the present procedure the temperature of the sample is appreciably lower than the thermostat temperature. The present technique must be modified in some manner to get better heat transfer, probably by pelletizing the cellulose sample. Experimental work on this phase of the problem is continuing. It should be mentioned that in the sorption experiments W_e as determined from the plot of t/W against t always checked the value of W_e obtained from equilibrium measurements to one per cent or better. As the equilibrium measurement is free from thermal effects caused by the evolution of heat it was concluded that the sorption measurements were being made sufficiently close to thermostat temperatures so as to be significant. The low energy of activation for the sorption process indicates that the change in k with change in temperature is about three per cent per degree in comparison to a change of greater than six per cent per degree usually encountered in kinetic work. This behaviour helps to minimize the temperature effect in the sorption experiments.

NUMBER OF SURFACE SITES

The kinetic data indicate that the number of surface sites on cellulose is small. The total number of moles of methanol held by cellulose at a given time must be equal to the moles of methanol on the surface plus the moles of methanol held in the interior. The experimental quantity is, of course, the total number

of moles. Kinetically, it would appear that the only manner in which the total number of moles could follow the experimental kinetic equations would be that the number of moles of methanol held in the interior is essentially equal to the total number of moles or that the moles of methanol adsorbed on the surface is small. If this is true, the number of effective surface sites on cellulose must be small. Experimental confirmation of this point is desirable.

The adsorption of tertiary butyl alcohol on cellulose has been measured at 45°C. Tertiary butyl alcohol was selected as a molecule having relatively large dimensions along the x, y and z axes. The sorption of tertiary butyl alcohol by cellulose is a very slow process, and equilibrium values were not obtained because of the slowness of the system to come to equilibrium. The following procedure was adopted assuming that surface adsorption had reached its equilibrium value in one hour. For non-porous solids ten minutes suffices. The cellulose sample was exposed for one hour to a known pressure of tertiary butyl alcohol and the increase in weight recorded. The sample was then evacuated overnight and a new weight increase measured for a new pressure. Under these conditions, the cellulose sample returns to its initial weight on pumping so that the adsorption is reversible. Measurements of this type were made from relative pressures 0·1 to 0·8 and gave a Langmuir type isotherm. Tertiary butyl alcohol adsorptions ranged from $1{\cdot}4 \times 10^{-5}$ to $7{\cdot}9 \times 10^{-5}$ moles alcohol per gramme cellulose. Except at low values of c, these values for tertiary butyl alcohol are much smaller than those obtained with methanol (see *Table 1*). These data are considered experimental evidence that the number of surface sites on the cellulose is small and that most of the methanol held by the cellulose is held on internal sites.

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Coal Research Laboratory, Department of Chemistry,
Carnegie Institute of Technology,
Pittsburgh 13, Pa

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*Sorption of Polar Vapours on Swelling Gels**

P. FUGASSI and G. OSTAPCHENKO

From an investigation of the kinetics of methanol sorption on coal, a new sorption isotherm has been derived of the form

$$W_e = AK\Sigma/(1 + K\Sigma)$$

$$\Sigma = K_1 p^0 c/[1 + (K_1 p^0 - 1)\, c][1 - c]$$

In these equations, W_e is the sorption usually expressed as moles of sorbed vapour per gramme of solid, c is the relative pressure of the vapour and p^0 is the vapour pressure of the liquefied vapour at the temperature in question. The equation has three adjustable parameters, A, K and K_1. The equation has been applied to the sorption of polar vapours by proteins, nylon and other swelling gels. The equation agrees with experiment over a range of relative pressures from 0·1 to 0·9 and also accounts for the effect of temperature changes.

RECENT kinetic investigations made in this laboratory on the sorption of gaseous methanol by coal[1] and cellulose[2] have shown that both coal and cellulose follow the same rate equation

$$W = k_x W_e^2 t/(1 + k_x W_e t)$$

In this equation W is the moles of alcohol taken up by one gramme of solid at time t, W_e is the corresponding value at infinite time, t is the time and k_x is the experimental velocity constant. On the basis of fragmentary data in the literature and unpublished data from this laboratory it appears that a rate equation of this form would be expected if the gas is a polar compound and if the solid is a swelling gel composed of oxygen-containing compounds.

For methanol sorption on cellulose the experimental velocity constant involves the fraction of surface sites holding two methanol molecules per site and from this fact the adsorption of methanol on the surface of cellulose is known to be of multilayer type. The dependence of k_x upon the surface sites holding two methanol molecules gave a new sorption equilibrium isotherm of the following type

$$W_e = AK\Sigma/(1 + K\Sigma) \quad \ldots\ldots [1]$$

$$\Sigma = K_1 p^0 c/[1 + (K_1 p^0 - 1)\, c][1 - c] \quad \ldots\ldots [2]$$

In equation 1, W_e is the equilibrium sorption in moles per gramme of solid at some fixed temperature, A is a constant being moles of interior sites per gramme of solid, and K is a dimensionless equilibrium constant. In equation 2, K_1 is an equilibrium constant (atm^{-1}) for the adsorption of methanol on surface

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sites, p^0 is the vapour pressure (atm) of the liquefied vapour at the temperature in question, and c is the relative pressure of the vapour.

The mechanism which leads to these equations is that vapour is rapidly adsorbed on the surface sites and then adsorbed molecules slowly migrate from the surface into the solid phase.

Equation 1 really gives the amount of vapour held in the interior of the solid. The total amount of vapour held by the solid is obviously the sum of two terms; the adsorption on the surface and the absorption in the interior. Thus

$$(W_e)_{\text{total}} = (W_e)_{\text{interior}} + (W_e)_{\text{surface}}$$

For the total amount of vapour held by the solid, which is the experimental quantity measured, the full equation is

$$(W_e)_{\text{total}} = AK\Sigma/(1 + K\Sigma) + B\text{f}(c) \quad \ldots . [3]$$

In equation 3, B represents moles of surface sites per gramme of solid.

The nature of f(c) is not completely known. If f(c) is Σ, the full equation would have four parameters: A, B, K_1 and K. However, Σ is really the adsorption equation for an infinite number of layers and approaches infinity as c approaches 1. For this reason f(c) must be a modified equation where adsorption is restricted to n layers. The use of a modified equation introduces five parameters and this number of parameters is meaningless when only equilibrium data are available. Kinetic data if available would permit independent evaluation of one of the parameters. However, such data are not available for most of the systems to be discussed here.

In applying the full equation 3 to the data in the literature the assumption will be made that B approaches zero. Experimentally there is evidence that in the case of methanol sorption on cellulose this assumption is valid. In this case the amount of methanol adsorption on the surface appears to be less than ten per cent of the total weight of methanol held by the cellulose. However, an assumption of this type would be expected to affect the behaviour of the equation at low values of c. Accordingly the discussion which follows uses the partial equation 1 and is limited to a range of relative pressures from 0·1 to higher values. Equation 1 will be applied to some of the data available in the literature on the sorption of polar molecules by swelling gels.

SORPTION OF WATER BY PROTEINS

A comprehensive study of water sorption by various proteins has been published by H. B. BULL[3]. He showed that the experimental data fitted the BET equation up to relative pressures of 0·4 to 0·5 excepting salmin where two different sets of constants in the BET equation were required. In general, application of the new equation shows that the experimental data are followed up to relative pressures of 0·9 or greater. A comparison of experimental and calculated values of W_e for the sorption of water on wool are given in *Table 1*. As previously mentioned the use of equation 3 would give better agreement at low values of c.

Table 1. Calculated and experimental values W_e—water on wool

c	$W_e \times 10^3$ (*expt*) *moles/gramme*	$W_e \times 10^3$ (*calc.*) *moles/gramme*	W_e (*calc.* − *expt*) *moles/gramme*
0·1	2·36	2·06	−0·3
0·2	3·47	3·56	+0·09
0·3	4·57	4·54	−0·03
0·5	6·35	6·38	+0·03
0·7	8·67	8·71	+0·04
0·9	12·52	12·46	−0·06

Equation 1 has three parameters: A, K and K_1. A tabulation of the values of these parameters for the sorption of water on various proteins is given in *Table 2*.

Table 2. Sorption of water on proteins[3]

Protein	K_1 (atm^{-1})		K		A (*moles sites/gramme*)	
	25°C	*40°C*	*25°C*	*40°C*	*25°C*	*40°C*
Wool	173·18	65·02	0·4133	0·4346	0·0155	0·0144
Gelatin	280·32	89·22	0·2500	0·3286	0·0289	0·0239
Collagen	315·56	85·04	0·2473	0·3057	0·0317	0·0273
β-*Lactoglobulin (crystals)*	182·67	71·99	0·2117	0·2157	0·0240	0·0225
Silk	213·53	80·03	0·2772	0·3038	0·0127	0·0113
C-Zein	305·67	114·72	0·1842	0·2401	0·0148	0·0118
B-Zein	283·47	132·86	0·2308	0·2363	0·0128	0·0115

The values of the equilibrium constant, K_1, in *Table 2* are for the reaction

$$H_2O(g) + S \rightleftharpoons S \cdot H_2O$$

In this equation S represents surface sites. It will be noted that K_1 always decreases as temperature increases. The heat of reaction associated with the change in K_1 can be calculated by conventional methods. When this is done it is found that the calculated heats of reaction range from 9400 to 16200 cal/mole and the average value is about 12000 cal/mole. It appears that the surface sites on various proteins are very similar as would be guessed from their similar chemical composition.

The values of K in *Table 2* are for the reaction

$$H_2O_{(surface)} + D \rightleftharpoons D \cdot H_2O$$

Here D represents interior sites. An increase in temperature gives an increase in K. However, the change is not great so that the heat of reaction is close to zero or in the extreme case about 3000 cal/mole endothermic. The values of A, which is moles of interior (D) sites per gramme of solid, show a small decrease with increase in temperature. The maximum change in A for a 15° temperature interval is of the order of 20 per cent. The average change in A

is about half of this. It would be anticipated that A would be independent of temperature or change slightly with the temperature.

In discussing Bull's results, L. PAULING[4] correlated the number of water molecules held in the first layer as calculated from the BET equation with the number of polar side groups present in the protein chain and found approximately a one-to-one correspondence. Taking Pauling's values for the moles of polar side groups per gramme of protein and dividing these values into the previously listed values for A, ratios are obtained ranging from 3 to 5. These ratios are interpreted as meaning that each polar side group introduces sufficient disorder into a protein lattice that 3 to 5 water molecules are held in these disordered regions. With this modification the mechanism of the sorption of polar molecules by proteins as deduced from the new isotherm is essentially identical with the concepts of Bull and Pauling.

SORPTION OF POLAR MOLECULES BY NYLON

Nylon is a condensation polymer of the polypeptide type with no polar side groups. In *Table 3* are listed the values of A, K and K_1 calculated for the sorption of various polar vapours on Nylon 66.

Table 3. Sorption of polar vapours on Nylon 66

Ref.	*Vapour*	*State*	$\frac{T}{°C}$	K_1 (atm^{-1})	K	A (*moles sites/gramme*)
3	H_2O	*Unstretched*	25	105·42	0·2184	0·00688
3	H_2O	*Unstretched*	40	27·63	0·3336	0·00551
3	H_2O	*Stretched*	25	95·56	0·3717	0·00473
3	H_2O	*Stretched*	40	31·24	0·4235	0·00417
5	H_2O	?	40	32·65	0·1825	0·00754
5	CH_3OH	?	25	12·66	0·1128	0·01412
5	C_2H_5OH	?	25	22·96	0·2240	0·00695
5	C_2H_5CN	?	25	30·15	0·2797	0·00116

For the results in *Table 3* it will be noted that the sorption of water by nylon is much less than the sorption of water by proteins as indicated by the lower values for A. The lower values for A for nylon indicate as is known from other evidence that nylon has a high degree of order or a low degree of disorder. Part of the disorder in nylon must arise from the fact that the chain length of the nylon polymer is much smaller than that in natural polymers. Each chain end can be considered as a disturbance centre in the vicinity of which disorder must occur. The molecular weights of the particular nylon samples are not known but if the chains have an average molecular weight of 10^4 then the number of disturbance centres would be 2×10^{-4} centres per gramme of nylon. From the protein data it appears that each polar side group or one disturbance centre furnishes sorption sites for 5 molecules of water. If we use the same assumption, the value of A for nylon would be 1×10^{-3} sites per gramme in comparison with the experimental value of 4 to 5×10^{-3} sites per gramme. Exact agreement would require an average molecular weight for nylon of 2000 to 2500.

In the disordered regions complete hydrogen bonding between adjacent chains has not taken place. Sorption is probably limited to such regions as it is unlikely that molecules of any vapour can permeate any region having high order. As shown from the data in *Table 3*, stretched nylon has lower disorder than the unstretched material.

It is interesting to note that the values of A vary with the nature of the vapour undergoing sorption. The value of A decreases in going down the series: CH_3OH, C_2H_5OH and C_2H_5CN. This change in A is probably caused by the increase in molecular size in going from CH_3OH to C_2H_5CN. In other words all types of disordered regions are present ranging from those which can only be permeated by CH_3OH to those sufficiently disarranged to accommodate all polar molecules whose size is equal to or less than that of the C_2H_5CN molecule. Although H_2O as a small molecule would be expected to permeate as many disordered regions as any other molecule nevertheless the A values indicate that it is not as good as CH_3OH but is better than C_2H_5OH. The reason for this discrepancy is not known but it may involve the fact that the H_2O molecule can be considered multifunctional with respect to hydrogen bonding if the spatial configuration is just right.

SORPTION OF METHANOL ON VARIOUS POLYMERS

The sorption of methanol on coal and other natural polymers has been under investigation in this laboratory for several years. These systems fit the sorption equilibrium isotherm. The values of A, K and K_1 are tabulated in *Table 4*.

Table 4. Sorption of methanol on natural polymers

Ref.	*Solid*	T °C	K_1 (atm^{-1})	K	A (*moles sites/gramme*)
2	*Cotton linters*	30	14·51	0·7472	0·00261
2	*Cotton linters*	35	13·60	0·6505	0·00265
2	*Cotton linters*	45	9·91	0·5844	0·00264
6	*Kincaid lignite*	45	18·57	0·8756	0·00768
6	*Wyoming coal*	45	14·71	0·8986	0·00640
1	*Pittsburgh coal*	35	29·55	1·1859	0·00172

The solids in *Table 4* have been listed in order of decreasing oxygen content. Cellulose is considered a precursor of coal and if cellulose is considered as the lowest rank coal having zero geologic age, then the solids are listed in order of increasing rank. It will be noted that A has at first a low value, rises to a high value and then decreases. The low value of A for cellulose is due to high order being present. With increasing age and rank order is destroyed and simultaneously oxygen content decreases. The low value of A for Pittsburgh seam coal is not due to order but arises from the small amount of oxygen-containing gel present in the coal.

Coal Research Laboratory, Department of Chemistry,
Carnegie Institute of Technology,
Pittsburgh 13, Pa

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The Determination of Phosphorus in Coal Ash

R. J. COSSTICK and H. N. S. SCHAFER

A new method has been developed for the extraction of phosphorus from coal ash, using hydrochloric and sulphuric acids, which gives results comparable with those obtained by the British Standard procedure using hydrofluoric and nitric acids. The phosphorus is then determined by an established colorimetric technique. The new method of extraction is simple, rapid, and well suited to routine batch analysis. It eliminates the need for costly platinum ware and avoids the disadvantages associated with the use of hydrofluoric acid.

RECENT ANALYTICAL TRENDS

THE accurate determination of the percentage of phosphorus in coal is particularly important if the coal is to be used for the manufacture of coke for the iron and steel industry or, alternatively, if it is to be burnt in a boiler. In the first case, the iron and steel produced may be of inferior quality if the phosphorus content exceeds 0·02 per cent, and in the second the phosphorus—liberated together with other inorganic constituents in the combustion process—may cause troublesome deposits and thus reduce steam output.

In the analysis of coal ash there has been of recent years a trend towards replacing many classical analytical procedures, including that for phosphorus determination, by more rapid methods based on the use of modern physical techniques. According to the British Standard Specification[1] for the determination of phosphorus in coal ash, the ash should be brought into solution using hydrofluoric and nitric acids and the phosphorus then determined by precipitation as ammonium phosphomolybdate followed by a titration procedure. The method is not suited to routine analysis, or to application by unskilled operators, because of the control required to obtain a precipitate of the correct composition. In addition, large quantities of ash, up to 1 g if the phosphorus content is low, are required for the analysis. In an endeavour to reduce the time required for the determination of phosphorus in coal and coke ash, R. BELCHER[2] introduced a semimicro colorimetric method. Belcher's method, while retaining the extraction process of the B.S. method, reduces the amount of ash required to 50 mg; this, in conjunction with the colorimetric determination of phosphorus as molybdenum blue, results in a considerable shortening of the analysis time. F. ELLINGTON and W. N. ADAMS[3] considered that the preparation of ash and the use of part of it for a phosphorus determination were disadvantages, and they proposed a method using coal as the starting material. The phosphorus is extracted by wet oxidation of the coal substance with sulphuric, nitric and perchloric acids, and then determined colorimetrically.

Ellington and Adams's method has been tested in these laboratories, but difficulties were experienced when applying the wet oxidation process to some

Australian coals (R. A. DURIE and H. N. S. SCHAFER[4]). In view of these difficulties, Belcher's extraction procedure was applied to the coal ash and Ellington and Adams's colorimetric method used for the determination of the phosphorus. Over the past few years numerous routine analyses have been carried out by this method and, although it represents a considerable improvement upon the B.S. procedure, experience shows that it has two disadvantages. First, in the extraction process great care must be taken in handling the extremely corrosive hydrofluoric acid; and, secondly, its presence demands the use of expensive platinum ware, which is not always readily available, particularly for routine tests.

THE PROPOSED NEW METHOD

These difficulties are avoided with the method described below, in which the phosphorus is extracted from the ash by boiling with concentrated hydrochloric acid, adding sulphuric acid, and heating the mixture till strong fumes are evolved. This treatment serves to separate the silica, which is removed by filtration after cooling and diluting with water. The filtrate is made up to a given volume, and an aliquot part is taken for the phosphorus determination by W. J. S. PRINGLE's[5] modification of Ellington and Adams's method.

The new method was applied to 16 coal ashes covering a wide range of phosphorus contents. For comparison purposes the same ashes were analysed

Table 1. Comparison of phosphorus determinations using (A) *British Standard method of extraction, and* (B) *proposed new method. Duplicate determinations by each of several operators*

All data on a per cent ash basis

Sample / Analyst	1		2		3		4	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1	1·15 1·24		1·28 1·32		0·96 0·96		0·62 0·62	
2	1·19 1·26	1·21 1·19	1·36 1·31	1·29 1·24	0·95 0·99	0·94 0·92	0·66 0·66	0·60 0·58
3	1·21 1·23		1·24 1·27		0·96 0·96		0·61 0·63	
4	1·14 1·19	1·18 1·19	1·21 1·33	1·22 1·23	0·89 0·94	0·90 0·90	0·61 0·61	0·58 0·58
5		1·20 1·14		1·28 1·24		0·93 0·91		0·60 0·54
Mean	1·20	1·19	1·29	1·25	0·95	0·92	0·63	0·58

Sample / Analyst	5		6		7		8	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1	0·35 0·40		0·33 0·34		0·25 0·27		— —	
2	0·37 0·38	0·37 0·36	0·34 0·35	0·34 0·33	0·28 —	0·27 0·25	0·19 0·17	0·18 0·17
3	0·35 0·37		0·33 0·33		0·23 0·26		0·18 0·18	
4	0·32 0·36	0·36 0·35	0·31 0·32	0·32 0·31		0·26 0·27	0·17 —	0·18 0·17
5		0·38 0·35		0·33 0·30		0·29 0·25		0·19 0·21
Mean	0·36	0·36	0·33	0·32	0·26	0·26	0·18	0·18

Table 1—continued

Sample / Analyst	9		10		11		12	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1	0·15 0·16		0·105 0·119		0·061 0·058		0·053 0·048	
2	0·16 0·16	0·15 0·14	0·097 0·107	0·090 0·091	0·051 0·058	0·043 0·043	0·044 0·046	0·030 0·033
3	0·14 0·16		0·093 0·097		0·047 0·048		0·040 0·042	
4	0·14 0·14	0·16 0·15	0·092 0·091	0·100 0·089	0·043 0·043	0·048 0·055	0·037 0·034	0·045 0·040
5		0·15 0·16		0·088 —		0·036 0·046		0·035 0·037
Mean	0·15	0·15	0·100	0·092	0·051	0·045	0·043	0·037

Sample / Analyst	13		14		15		16	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1	0·030 0·032		0·055 0·054		0·055 0·051		— —	
2	0·020 0·023	0·011 0·011	— —	0·040 0·040	0·036 0·054	0·036 0·035	0·028 0·032	0·011 0·012
3	0·018 0·022		0·048 0·056		0·042 0·045		0·025 0·026	
4	0·016 0·012	0·018 0·015	0·045 0·045	0·043 0·045	0·045 0·038	0·040 0·041	0·016 0·013	0·017 0·018
5		0·012 —		0·055 0·047		0·042 0·048		0·025 0·012
Mean	0·022	0·013	0·050	0·050	0·047	0·040	0·023	0·016

for phosphorus using hydrofluoric–nitric acid extraction as in Belcher's method, and determining the phosphorus by the usual colorimetric procedure. Five operators took part in the comparison test. On most samples, four of them made duplicate analyses using the hydrofluoric–nitric acid extraction procedure and three made duplicate analyses with the hydrochloric acid extraction. The results of all these analyses are shown in *Table 1.*

DISCUSSION

The agreement of the averaged results obtained by the two methods of extraction for each of the 16 samples is good and the differences between the averages are within accepted analytical tolerances. However, application of Student's *t* test (W. J. YOUDEN[6]) to the data shows that the differences between the means for some samples are statistically significant at the 95 per cent level. In these cases the value obtained by the hydrofluoric–nitric acid extraction is slightly higher than with the hydrochloric acid extraction. This indicates that with these samples the former treatment extracts phosphorus a little more efficiently than the latter. However, the difference is not of analytical significance and is more obvious with samples of very low than of high phosphorus content.

Summing up, the hydrochloric acid extraction procedure gives reproducible and reliable results, is suited to routine batch analysis, and can be carried out by relatively unskilled operators. It obviates the use of hydrofluoric acid and hence of platinum ware, two important factors from the point of view of laboratory safety and expense.

EXPERIMENTAL DETAILS

Reagents

Hydrochloric acid	10N
Sulphuric acid	18N and 5N
Nitric acid	15N
Hydrofluoric acid	40 per cent
Sodium hydroxide	5N
Ammonium molybdate	1 per cent w/v solution of $(NH_4)_6\ Mo_7\ O_{24} \cdot 4H_2O$
Reducing solution	0·3 per cent hydrazine sulphate, 1 per cent w/v sodium metabisulphite

Extraction of phosphorus

(a) *Belcher's*[2] *method*—Transfer 50 mg of ash to a platinum crucible, add 2 ml of 15N nitric acid and 1 ml of 40 per cent hydrofluoric acid. Evaporate to dryness on a sand bath. Repeat this operation, then add 1 ml of 15N nitric acid and evaporate to dryness. Add 5 ml of 5N sulphuric acid, digest to dissolve the soluble material, filter through a Whatman No. 40 paper into a 50 ml volumetric flask, wash the paper several times with warm water, cool and dilute to the mark. Run a blank consisting of the acids only, at the same time as the samples.

(b) *Proposed method*—Transfer 50 mg of finely ground ash to a 300 ml conical beaker and add 10 ml of 10N hydrochloric acid. While swirling the flask, boil over an open flame for 1 to 2 minutes. Place the beaker on a hotplate and continue the boiling for 2 to 3 minutes. Then add 10 ml of 18N sulphuric acid and evaporate until strong fumes are evident. Cool the beaker, dilute to about 20 ml, and boil the contents for a few minutes to dissolve any soluble residue. Remove the silica by filtration through a Whatman No. 541 paper, collecting the filtrate in a 100 ml volumetric flask. Rinse the beaker and wash the residue on the paper with distilled water. Finally, dilute to the mark. Run a blank consisting of the acids only, at the same time as the samples.

Determination of phosphorus

The procedure is as follows. Pipette a 10 ml aliquot part for method (a) plus 10 ml distilled water *or* 20 ml aliquot in method (b) into a 100 ml conical flask, add 8 ml of 5N sodium hydroxide, neutralize to the end point of phenolphthalein with 5N sulphuric acid, and add 7·5 ml in excess. Add 2 ml of reducing solution and 5 ml of 1 per cent ammonium molybdate. Mix well, and heat on a boiling water bath for 15 minutes. Cool, transfer to a 50 ml volumetric flask, and dilute to the mark. Mix well. Measure the optical density of 'molybdenum blue' in a 1 cm cell at 830 mμ using a spectrophotometer, or in a colorimeter using a suitable filter. Read the concentration of phosphorus in microgrammes from standard calibration curves prepared by treating known amounts of phosphate by the above procedures and plotting optical density against phosphorus concentration. Use the blank solution as the reference solution in all optical-density measurements.

With coals having high phosphorus contents it may be necessary to take a smaller aliquot, in which case the volume should be made up to 20 ml before proceeding as above.

Thanks are due to Dr R. A. Durie for assistance with the statistical treatment and for discussions of the results, and to M. S. Burns for supervision of the application of the extraction procedure under routine conditions.

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Coal Research Section,
Commonwealth Scientific and Industrial
Research Organization, P.O. Box 3,
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Determination of Hydroxyl Groups in Model Compounds, Coal and Coal Extracts

A. HALLEUX, S. DELAVARENNE and H. TSCHAMLER

A wide scatter of experimental results is observed when one standard sample of vitrain is analysed for hydroxyl groups by different methods. However, some measure of agreement is found between the results obtained by acetylation (in pyridine), and those derived from trimethylsilylether formation. Acetylation was further investigated in some detail on a series of twenty model compounds in order to gain a better understanding of its scope and limitations when used on coal. Although usually satisfactory, it sometimes suffers side reactions and incomplete reaction was also observed in a few instances. Notwithstanding these difficulties, acetylation presents the advantage of reproducibility and self-consistency, when the method is applied to a series of coal extracts.

THE importance of the role played by organically bound oxygen in the structure and properties of coals has been recognized for many years and special stress has been laid by several authors on the influence of oxygen on coking capacity[1–3]. It is therefore not surprising that efforts have been made, especially in recent years, to set up analytical methods of general application for determination of various oxygen-containing functional groups in coals. General surveys[4, 5] have been published which show the particular difficulties encountered in obtaining even semi-quantitative results in this field.

Significant advances have, however, been made, particularly in the development of methods for the determination of hydroxyl groups. Several of them are currently being used: (*1*) ion-exchange using barium hydroxide[5], (*2*) acetylation[4, 6–8], (*3*) direct acid–base titration[9], (*4*) silylether formation[10]. Still, a wide scatter of experimental results is evident in the literature as seen in *Figure 1*. (This figure is meant as an illustration of the different results and is admittedly schematic. It should not be used directly to read off what any one worker found for coal of given carbon content.)

It has been the aim of the present work to contribute to the evaluation of some of these methods, especially with application to the range of bituminous coals where hydroxyl groups may be considered to be essentially phenolic. In order to have a basis for comparison, a standard sample of vitrain was first subdivided and sent to several laboratories for analysis according to the methods commonly used in each of them. Results are listed in *Table 1*.

It is evident from *Table 1* that discrepancies exist between the results obtained in the different laboratories, both for elementary analysis (especially carbon) and for hydroxyl content. The best agreement for the elementary analyses is found between 1, 2, 3 and 7. They were therefore taken as correct

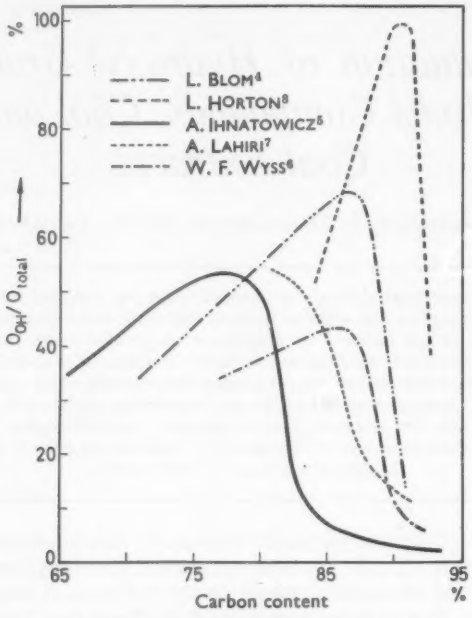


Figure 1. Comparison of hydroxyl determinations by various workers (schematic)

within experimental error. Hydroxyl content was determined by acetylation in 3, 4, 5 and 7. The high value found in 3 is due to the reaction temperature of 140°C which is 40° higher than that used in 4, 5 and 7. We believe that the former procedure[7] may be responsible for side reactions, at the same time as it favours completeness of reaction (see below). The danger is at least partly reduced in the method of L. BLOM, L. EDELHAUSEN and D. W. VAN KREVELEN[4] used in 4 and 7. The result found in 5, although lower than that of 4 and 7 is not sufficiently different to warrant any clear-cut decision concerning possible incompleteness of the reaction. The method used in 6 is clearly unsuitable for complete titration of —OH groups in the whole range of bituminous coals especially on account of poor contact of the reagent. Finally, the value given in 2 was obtained by the method of trimethylsilylether formation[10]. The agreement observed between the latter and the results 4 and 7 is especially gratifying because of the difference in the chemical methods used. Absence of appreciable interference by side reactions is strongly indicated in this case, since the possibility that they would be the same in silylation and acetylation is extremely unlikely.

(A) DETERMINATION OF HYDROXYL GROUPS IN MODEL COMPOUNDS BY ACETYLATION

Following the general observations made above, we have felt it necessary to investigate acetylation in some detail in order to gain a better understanding

Table 1. Analysis of a standard sample of anthraxylon (Majestic Mine, Kentucky, Pike County, Pond Creek)

Laboratory	Ash	Moisture	Elementary analysis (m.a.f.) %					% O_{OH} (m.a.f.)	% $\frac{O_{OH}}{O_{total}}$	Method used
			C	H	N	S	O			
1. *U.C.C. Olefins Co. (U.S.A.)*	2·4	2·08	85·96	5·27	1·45	0·68	6·64	—	—	
2. *U.S. Bureau of Mines (U.S.A.)*	2·0	1·9	86·5	5·2	0·8	0·7	6·8	3·31	49	*Trimethylsilylether formation*[10]
3. *Central Fuel Res. Inst. (India)*	2·40	2·85	86·4	5·2	1·5		6·9*	4·70	68	$(CH_3CO)_2O$ + CH_3COONa *at 140°C*[7]
4. *Staatsmijnen in Limburg (Holland)*	—	—	87·8	5·4	—	—	6·0	3·8	63	$(CH_3CO)_2O$ + *pyridine at 100°C*[4]
5. *B.C.U.R.A. (England)*	—	—	—	—	—	—	—	2·94	44†	$(CH_3CO)_2O$ + *pyridine at 100°C*[6]
6. *Glowny Instytutu Gornictwa (Poland)*	—	—	81·9‡	5·3‡	—	—	—	0·0 1·85‡§	0 28†	*Ion exchange*[5] *with* $Ba(OH)_2$
7. *E.R.A.*	2·9	2·0	86·0	5·2	2·1*		6·7	3·7	55	$(CH_3CO)_2O$ + *pyridine at 100°C*[4]

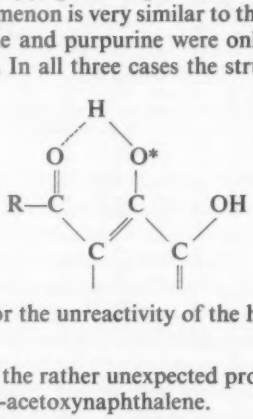
* By difference. † Calculated by using 6·7% O_{total}. ‡ M.f. instead of m.a.f. § After mild hydrolysis.

of its scope and limitations. For this purpose we have applied the procedure of van Krevelen and co-workers[4] to twenty model compounds which are listed in *Table 2*, together with the results of acetylation as regards the qualitative nature of the material isolated after treatment. The derivatives isolated after acetylation were purified and identified by elementary analysis, melting point, and infra-red (i.r.) spectroscopy. Where doubt was possible concerning the number of acetoxy groups, hydrolysis of the acetylated derivative was carried out.

On examination of *Table 2*, it is seen that complete acetylation was observed in the majority of cases, but that examples of complete failure to react and of incomplete acetylation were both found. Furthermore, two interesting examples of side reactions occurred. One leads to the disappearance of hydroxyl groups whereas the second results in an increase in the number of these groups.

In compounds of type (*a*), only the very hindered phenols remained unacetylated. But with 2,6-di-*tert*-butylphenol, where the *para* position is free, oxidation to the corresponding diphenoquinone prevented recuperation of the starting material except if air was rigorously excluded during the reaction.

In compounds of type (*b*), gallacetophenone was only acetylated in the 3,4-positions. This phenomenon is very similar to that observed in compounds of type (*c*) where alizarine and purpurine were only acetylated in the 2- and 2,4-positions respectively. In all three cases the structure



seems to be responsible for the unreactivity of the hydroxyl group marked by an asterisk.

Naphthazarine showed the rather unexpected property of being reductively acetylated to 1,4,5,8-tetra-acetoxynaphthalene.

Of the two ketones studied, benzoin enolizes in the acetic anhydride–pyridine medium and yields α,α′-diacetoxystilbene, whereas dibenzoylmethane, which from i.r. evidence is nearly 100 per cent enolized in pyridine, remains unacetylated.

Quercetin is acetylated in the 3, 7, 3′, 4′-positions.

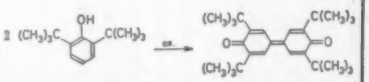
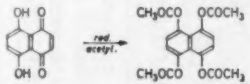
Failure to achieve complete acetylation can sometimes be corrected by increasing the reaction temperature, as we have found with alizarine at 115°C.

The increase in reaction temperature, however, compounds the danger of side reactions. A change of procedure does not solve this difficulty: acetylation by acetic anhydride/sodium acetate also leads to undesirable side effects, for instance in the presence of quinone groupings (phenanthraquinone, used as

Table 2. Treatment of models with $(CH_3CO)_2O$/pyridine at 100°C for 24 h

Empirical		Expected for		Found by analysis		MP		MP lit.		Remarks

Table 2. Treatment of models with $(CH_3CO)_2O$/pyridine at 100°C for 24 h

Compound	*Empirical formula*	*MP*	*Expected for complete acetylation*	*Found by analysis*	*MP*	*MP lit.*	*Remarks*
(a) *Simple phenols*							
Pyrogallol	$C_6H_3(OH)_3$	134	$C_6H_3(OCOCH_3)_3$	$C_6H_3(OCOCH_3)_3$	166	165	
2,6-Di-tert-butyl phenol	$C_{14}H_{21}OH$	37	$C_{14}H_{21}OCOCH_3$	$C_{28}H_{40}O_2$	245	239	
2,4,6-Tri-tert-butyl phenol	$C_{18}H_{29}OH$	130	$C_{18}H_{29}OCOCH_3$		130		*Starting material*
α-Naphthol	$C_{10}H_7OH$	96	$C_{10}H_7OCOCH_3$	$C_{10}H_7OCOCH_3$	43·5	44	
β-Naphthol	$C_{10}H_7OH$	122	$C_{10}H_7OCOCH_3$	$C_{10}H_7OCOCH_3$	70·5	69	
(b) *Intramolecular hydrogen-bonded phenols containing 6-membered chelate rings*							
Gallacetophenone	$C_8H_3O(OH)_3$	173	$C_8H_3O(OCOCH_3)_3$	$C_8H_3O_3(OCOCH_3)_3$	106	—	*Not completely acetylated*
2,4-Dioxybenzophenone	$C_{13}H_9O(OH)_3$	144	$C_{13}H_9O(OCOCH_3)_3$	$C_{13}H_9O(OCOCH_3)_3$	75	76	
2-Oxy-4-methoxy-benzophenone	$C_{14}H_{11}O_3(OH)$	63·5	$C_{14}H_{11}O_3(OCOCH_3)$	$C_{14}H_{11}O_3(OCOCH_3)$	75	—	
2, 2', 4, 4'-Tetroxy-benzophenone	$C_{13}H_8O(OH)_4$	197·5	$C_{13}H_8O(OCOCH_3)_4$	$C_{13}H_8O(OCOCH_3)_4$	136	—	
2,2'-Dioxy-4,4'-dimethoxy-benzophenone	$C_{15}H_{12}O_5(OH)_2$	122	$C_{15}H_{12}O_5(OCOCH_3)_2$	$C_{15}H_{12}O_5(OCOCH_3)_2$	127·5	—	
(c) *Intramolecular hydrogen-bonded oxyquinones containing 6-membered chelate rings*							
5,8-Dioxy-1,4-naphthoquinone (naphthazarine)	$C_{10}H_4O_4(OH)_2$	281	$C_{10}H_4O_4(OCOCH_3)_2$	$C_{10}H_4(OCOCH_3)_4$	265	270	
1,4-Dioxyanthraquinone (quinizarine)	$C_{14}H_6O_4(OH)_2$	194	$C_{14}H_6O_4(OCOCH_3)_2$	$C_{14}H_6O_4(OCOCH_3)_2$	201	200	
1,8-Dioxyanthraquinone (chrysazine)	$C_{14}H_6O_4(OH)_2$	191·5	$C_{14}H_6O_4(OCOCH_3)_2$	$C_{14}H_6O_4(OCOCH_3)_2$	244	230	
1,2-Dioxyanthraquinone (alizarine)	$C_{14}H_6O_4(OH)_2$	288	$C_{14}H_6O_4(OCOCH_3)_2$	$C_{14}H_7O_4(OCOCH_3)$	198	198 *to* 199	*Not completely acetylated*
1,2,4-Trioxyanthraquinone (purpurine)	$C_{14}H_5O_5(OH)_3$	259	$C_{14}H_5O_5(OCOCH_3)_3$	$C_{14}H_6O_4(OCOCH_3)_2$	204	203 *to* 205	*Not completely acetylated*
1,2,5,8-Tetroxyanthraquinone (quinalizarine)	$C_{14}H_4O_4(OH)_4$	275 *dec.*	$C_{14}H_4O_4(OCOCH_3)_4$	$C_{14}H_4O_4(OCOCH_3)_4$	201	200	
11,12-Dioxy-tetracene-9,10-quinone	$C_{18}H_8O_4(OH)_2$	346·5	$C_{18}H_8O_4(OCOCH_3)_2$	$C_{18}H_8O_4(OCOCH_3)_2$	264	260	
(d) *Miscellaneous*							
Dibenzoylmethane	$C_{15}H_{12}O_2$	77	$C_{15}H_{11}O(OCOCH_3)$		75·5		*Starting material*
Benzoin	$C_{14}H_{12}O(OH)$	135	$C_{14}H_{12}(OCOCH_3)_2$	$C_{14}H_{12}(OCOCH_3)_2$	82·5 127·5	83 (cis) 127·5	*Mixture of* cis *and* trans *diacetoxystilbene*
3,5,7,3',4'-Pentoxyflavone (quercetin)	$C_{15}H_5O_4(OH)_5$	310 *dec.*	$C_{15}H_5O_4(OCOCH_3)_5$	$C_{15}H_6O_2(OCOCH_3)_4$	200	193 *to* 195	*Not completely acetylated*

a model, gave rise to five different products, among which was found 9,10-diacetoxyphenanthrene).

The work which we have carried out on models shows that even a mild procedure for the acetylation of hydroxyl groups may lead to undesirable side effects, while on the other hand completeness of reaction is not guaranteed in all cases. Of course, a certain over-emphasis of difficulties is unavoidable in the presentation of results based as above on a limited and more or less arbitrary set of model compounds in which unfavourable features are probably more significant than in coal itself. Still, the objections must be borne in mind. A duplicate determination of hydroxyl groups by an independent method such as possibly that of the U.S. Bureau of Mines[10] is highly advisable on coals.

(B) ACETYLATION OF A VITRAIN AND ITS EXTRACTS

Notwithstanding a potential lack of accuracy, which can be at least partially corrected by a check with an independent method, acetylation presents the advantage of reproducibility and self-consistency. A sample of a high volatile A bituminous coal (*Table 3*) was progressively extracted with pyridine, 1,2,4-trichlorobenzene, benzene and carbon tetrachloride (i.e. each soluble part extracted with the next solvent in the above mentioned order). Each extraction was carried out in boiling solvent for 24 hours under nitrogen. The ratio of material to solvent was 10 g/l., in all cases.

Table 3. Analysis of anthraxylon, Pittsburg bed, U.S. experimental mine, Bruceton, Allegheny County, Pa

Component	(*Vitrinite content: 94%*)
Moisture	2·6%
Ash	2·5%
Volatile matter	34·3% (*m.a.f.*)
C	83·9% (*m.a.f.*)
H	5·3% (*m.a.f.*)
O	8·2% (*m.a.f.*)
(N + S)	2·6% (*by difference*)

The hydroxyl content of the vitrain and its extracts was measured by the method of van Krevelen and co-workers[4]. Results are listed in *Table 4*.

We have found that experimental results for O_{OH} are usually reproducible within 2 per cent. The data in column 4 (*Table 4*) are calculated values on the basis of the extraction yields. For example

$$\%\ (O_{OH})_{vitrain} = (27 \times 3{\cdot}5 + 73 \times 4{\cdot}3)/100 = 4{\cdot}1$$

These values are in reasonably good agreement with the experimental ones if all causes of error are taken into account. Therefore the method leads to self-consistent results.

In the course of the work on acetylation of coal and coal extracts, several observations of interest have been made. Two points in the acetylation procedure of Blom, Edelhausen and van Krevelen[4] are in need of further study:

(*1*) the precipitation of the acetylated material in water to decompose excess acetic anhydride is not altogether quantitative, even after long standing of the aqueous suspension; (*2*) hydrolysis of the acetylated samples is a slow process which in some cases takes more time than prescribed, as can be shown by i.r. spectroscopy on samples after hydrolysis.

Table 4. Hydroxyl content of vitrain and its extracts

Sample	% O_{OH}	*Extraction yield per cent*	% O_{OH} *calc.*
Vitrain	4·0	—	4·1
Pyridine-soluble	3·5	27	3·6
Pyridine-insoluble	4·3	73	
$C_6H_3Cl_3$-*soluble*	1·1	35	1·3
$C_6H_3Cl_3$-*insoluble*	4·9	65	
Benzene-soluble	1·5	48	1·8
Benzene-insoluble	1·0	52	
CCl_4-*soluble*	1·5	75	1·8
CCl_4-*insoluble*	3·2	25	

Furthermore, we have noticed that acetylation of the vitrain used decreases the percentage of ash in the samples [2·5 per cent ash (m.f.) before and 1·9 per cent (m.f.) after acetylation]. The remainder stays behind in the water which has been used in the flocculation of the acetylated sample. Qualitative analysis of the ash by emission spectroscopy, however, indicates that its composition stays approximately the same all through the treatment.

Acetylated samples of coal extracts seem to aggregate less in solution than unacetylated ones. At least their tendency to flocculate out of solution is diminished. They are also more resistant to air oxidation at moderate temperatures. This observation which is in agreement with the findings of others[11] was substantiated by our paramagnetic resonance measurements.

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Extraction Experiments on Coal with Various Pyridine Bases

A. HALLEUX and H. TSCHAMLER

A study of coal extraction with a series of closely related pyridine bases and comparison of results with the sequence of basic strength of these bases towards mineral acids, trimethylboron, and phenols indicates that acid–base interaction is sufficient to explain the relative solvation power of pyridine bases for coal; allowance must be made for steric interaction between the solvent and substituents surrounding the acid sites in coal, but the strain need not be very large to account for the observed phenomena.

IT has become increasingly evident in recent years that appreciable solvation of coal at moderate temperatures can only be accomplished by solvents having the common property of being electron donors. Particularly active in swelling and peptizing coal are the primary aliphatic amines up to *n*-dodecylamine, and secondary or tertiary heterocyclic amines[1–3]. The possibility of a chemically specific interaction between these solvents and the coal substrate has been recognized[2, 3], and its significance for the interpretation of the mechanism of coal dispersion in solvents of this type has been discussed[2]. The sum of available evidence points to a general acid–base relationship, through hydrogen-bonding between the solvent acting as a Lewis base and the acid sites present in the coal structure, in spite of several discrepancies which have prevented a completely satisfactory interpretation of the observed phenomena[1, 2]. Indeed, the contradictions which have come to light are probably more apparent than real, and arise from the intrinsic difficulties encountered whenever an attempt is made to find a close correlation between acid–base interactions of quite different nature, and for a wide variety of electron donor molecules[4]. In particular, the failure to find a general trend of linear nature between coal swelling in different solvents[2] and the infra-red (i.r.) OD-stretching frequency shifts of methanol-d in these same solvents[5] is undoubtedly due to the choice of solvents insufficiently alike with regard to coal. Again, the fact that such a linear relationship was previously found for wood[6] is an indication that the acid–base interactions involved are more closely related than in the case of coal.

Furthermore, Lewis acid–base equilibria have been shown to be strongly dependent on the *mutual* steric interaction of the partners[7], and this phenomenon is certainly involved in systems coal/solvent also, as has been pointed out by I. G. C. DRYDEN[1, 2]. The difficulty here resides in knowing how steric effects are going to affect the acid–base equilibrium, since the configuration surrounding the acid sites in coal is unknown. This may also lead to apparent anomalies when the behaviour of coal towards organic bases (e.g. ammonia and the methylamines) is compared with the latter's properties towards model acids such as the boron alkyls[1].

It has been the aim of the present work to measure, on the basis of extraction yields, solvation of coal by several *closely related* pyridine bases, and to compare the results with the behaviour of the latter towards a set of model phenols. In this way, we have been able to show that the relation between electron availability of the solvent base and solvation power for coal is satisfactorily coherent (see below).

Table 1. Analysis of anthraxylon, Pittsburgh bed, U.S. experimental mine, Bruceton, Allegheny County, Pa

Component	*(Vitrinite content: 94%)*
Moisture	2·6%
Ash	2·5%
Volatile matter	34·3% (*m.a.f.*)
C	83·9% (*m.a.f.*)
H	5·3% (*m.a.f.*)
O	8·2% (*m.a.f.*)
(N + S)	2·6% (*by difference*)

Samples of a vitrain (see *Table 1*) were extracted with pyridine, 2,6-lutidine, 3,5-lutidine and 2,6-di-*tert*-butylpyridine under standard conditions (24 h, under nitrogen, coal to solvent ratio: 1 g/100 ml) and at *corresponding temperatures* relative to the boiling point of each solvent. Furthermore, a pyridine extract of the same vitrain was also extracted with the same solvents. Extraction yields are listed in *Tables 2* and *3*.

Table 2. Extraction yields of vitrain sample

Solvent	*Temperature of extraction °C*	*Yield per cent*	*% Yield relative to pyridine*
Pyridine	67	24	100
2,6-Lutidine	91	17	70
3,5-Lutidine	115	34	140
2,6-Di-tert-butylpyridine	150	2	8

Table 3. Extraction yields of pyridine extract

Solvent	*Temperature of extraction °C*	*Yield per cent*
Pyridine	20	100
2,6-Lutidine	39	69
3,5-Lutidine	63	100
2,6-Di-tert-butylpyridine	91	<15

On the other hand, the following basicity sequences are known for the pyridine bases under study:
(*1*) pK_a[8]:

2,6-di-*tert*-butylpyridine < pyridine < 3,5-lutidine < 2,6-lutidine

The position of 3,5-lutidine in the pK_a series has not been determined experimentally by H. C. Brown, but has been established by us, at the same time as we remeasured pyridine and 2,6-lutidine. The pK_as (25°C; 50 per cent ethanol–water) are: pyridine 4·47, 3,5-lutidine 5·20 and 2,6-lutidine 5·64.

(*2*) *Stability of trimethylboron coordination complex*[7]:

2,6-di-*tert*-butylpyridine $\simeq$ 2,6-lutidine $\ll$ pyridine $<$ 3,5-lutidine

The position of 3,5-lutidine in the trimethylboron complex series has not been determined experimentally but may be estimated from the following sequence:

pyridine $<$ 3-methylpyridine[9]

The position of 2,6-di-*tert*-butylpyridine may be inferred from results obtained with boron trifluoride[8].

Furthermore, we ourselves have determined the stability of the hydrogen-bonded complexes formed in carbon tetrachloride between phenol and the various pyridines. For this purpose, we have calculated the equilibrium constant

$$K = x/(a - x)(b - x)$$

where x is the concentration of hydrogen-bonded complex; $(a - x)$ and $(b - x)$ are the concentrations of free phenol and base respectively, a and b representing the initial concentrations of phenol and base. The experimental determination of $(a - x)$ was carried out by i.r. spectroscopy, using the OH-stretching frequency of monomeric phenol. Concentrations were chosen so as to insure that phenol in carbon tetrachloride is completely in monomeric form. This was achieved when a was lower than 0·025 M. Results are listed in *Table 4*.

Table 4. Equilibrium constants for interaction between phenol and various pyridine bases (at room temperature)

Pyridine base	K(*l. mole*$^{-1}$)
Pyridine	43±3
2,6-Lutidine	78±4
3,5-Lutidine	107±7
*2,6-Di-*tert*-butylpyridine*	3±2

Comparison between the values listed in *Tables 2*, *3* and *4* and the basicity sequences (1) and (2) shows that coal extraction yields cannot be correlated exactly with either the pK_a values of the bases or their interaction constants with trimethylboron or phenol. The pK_a sequence reflects the electron availability of the pyridines for the proton, an acid of negligible steric requirements. On the contrary, complex formation with trimethylboron is strongly influenced by steric factors. Hydrogen bond formation with phenol has only weak steric requirements since the stability of the complexes is qualitatively in the same order as the pK_as of the bases, except for the inversion of 2,6- and 3,5-lutidine (*Table 4*). On the other hand, the sequence of extraction

yields on coal (*Table 2*) is *qualitatively* the same as that which one obtains in the trimethylboron complexes. However, in the latter, there is *no* complex formed with 2,6-lutidine and 2,6-di-*tert*-butylpyridine, whereas a significant extraction yield for coal is still obtained with 2,6-lutidine. Thus, we may conclude that the interaction between coal and the pyridine bases has less stringent steric requirements than the trimethylboron complex formation, while it still is more sensitive to steric hindrance than hydrogen bond formation with phenol. A better model than phenol may possibly be found in an *ortho*-substituted phenol such as 2-methylphenol or 2,6-dimethylphenol. In this case we can expect to have K values parallel to the extraction yields on coal. This view is partly supported by the K values reported for 2-methylphenol, with pyridine and 2-methylpyridine[10] (K at 25°C for pyridine: 35, for 2-methylpyridine: 29).

Our results confirm the hypothesis put forward by I. G. C. Dryden that the nature of the interaction between specific solvents and coal is linked with the availability of a free electron-pair in the solvent molecule. They offer experimental evidence that the latter is involved in hydrogen-bonding with acid sites in the coal and that solvation power follows the hydrogen-bonding ability of the solvent as governed by electronic and steric effects of substituents. There is some indication that the front strain involved in the coal–solvent interaction is not quite as large as conclusions derived from experiments with aliphatic amines[2] would lead one to expect. However, the fact that a discrepancy exists probably indicates that no completely satisfactory model system has as yet been found for the steric environment of the acid sites in coal.

Finally it must be noted that the interpretation of observations made on a closely related series of pyridine bases must be considered as tentative on account of the complexity of solvation processes and the largely unknown structure of coal.

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Brussels, Belgium

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The Inorganic Constituents in Australian Coals I—The Direct Determination of the Total Mineral-matter Content

H. R. Brown, R. A. Durie and H. N. S. Schafer

The application to Australian coals of two direct methods of determining total mineral-matter content is described, one being non-destructive and the other destructive with respect to the mineral matter. The non-destructive method is based on low-temperature oxidation of the organic coal substance and appears to be the first attempt to apply such an approach to mineral-matter determination in coal. The second method is based on acid digestion and is an adaptation of a procedure already described in the literature. A comparison of the two methods confirms that they give closely comparable results but that for routine application the one based on low-temperature oxidation is to be preferred. Relative merits and possible complicating factors are discussed. The King–Maries–Crossley formula cannot always be relied upon to give precise estimates of the mineral-matter content of Australian coals.

In the classification and utilization of coal the quantity and types of inorganic (mineral) matter present are of importance. Quantitatively the ash yield differs from the amount of mineral matter present, owing to loss of lattice water from hydrated minerals, the decomposition of carbonates, and the oxidation of sulphides during the ashing procedure. Thus a reliable direct method for estimating the total quantity of mineral matter present in coal is desirable, particularly for application to coals rich in mineral matter.

In the absence of such a method the normal practice has been to make use of deductions based on the ash yield and analytical data for the ash and the coal, for which purpose many empirical formulae have been proposed. In the United Kingdom and Europe the (KMC) formula due to J. G. King, M. B. Maries and H. E. Crossley[1] is generally regarded as the best since it is based soundly on a knowledge of the nature of the thermal degradation of the predominant coal minerals during the standard ashing procedure. However, all such empirical formulae are open to the criticism that they make no allowance for the possible variation of mineral types throughout any one seam or from one seam to another, and thus cannot be expected to yield reliable values for the mineral-matter content of every coal sample.

Recently W. Radmacher and P. Mohrhauer[2] published details of a direct method which appeared to be relatively simple and capable of yielding results for the mineral matter in Ruhr coals that were at least comparable with results calculated from the KMC[1] formula. The method is based on acid digestion of the minerals in a coal sample under conditions which cause no attack on the coal substance itself. This approach is not new (e.g. K. Mayer[3]), but Radmacher and Mohrhauer appear to have succeeded in establishing satisfactory conditions for the acid digestion. A recent application of this method to some British coals has received favourable comment (M. Bishop and D. L. Ward[4]).

The acid digestion method is destructive with respect to the minerals present, and it is of interest to consider as an alternative the possibility of isolating the mineral matter intact and weighing it directly. The most promising approach would appear to be that of complete removal of the coal substance by low-temperature oxidation with no change in the majority of the minerals present in the coal and with only predictable changes in the remainder.

For the purposes of X-ray diffraction studies, a temperature of about 380°C has been used by various workers to isolate the mineral matter in air-borne dusts in mines (G. NAGELSCHMIDT[5]), in roof clods and coal samples (D. HICKS and G. NAGELSCHMIDT[6]), and in coals and slurries of moderate and high ash contents. Quartz, clay minerals (kaolinite, mica) and carbonate minerals (calcite, ankerite) were identified unchanged, with respect to the X-ray diffraction pattern, in the oxidation residues. Although J. B. NELSON[7], D. FLINT[8], and more recently W. GUMZ[9] have commented favourably on the potentialities of low-temperature oxidation for the direct determination of the quantity of mineral matter present in coal, there are no reports of a systematic investigation of the technique for this purpose.

The present authors have made a parallel investigation of both the acid digestion and the low-temperature oxidation techniques for the direct determination of the mineral-matter content of some Australian coals. Previous assessments of the acid-digestion method[2, 4] have used the quantity of mineral matter as calculated with the KMC formula for comparison. For reasons already stated, values so calculated are not reliable standards and it was considered that an intercomparison of the results obtained with the direct methods would provide a more reliable test of each method and assist in locating the cause of any differences. The general reliability of the KMC formula when applied to Australian coals was also investigated.

GENERAL CONSIDERATION OF EXPERIMENTAL CONDITIONS

Low-temperature oxidation (non-destructive) method

Available data on Australian coals are in general agreement with Nelson's[7] statement that hydrated silicate minerals (clay minerals), sulphides and carbonates together account for more than 95 per cent of the mineral matter associated with most coals. It has been shown by petrographic and X-ray diffraction work that kaolinite is the predominant clay mineral in coals from New South Wales and the presence of illite and quartz, as well as of pyrite, ankerite and siderite, has been reported (C.S.I.R.O. Coal Research Section, unpublished data). Recent X-ray diffraction studies (R. E. GRIM[10]) have shown that montmorillonite is generally the predominant clay mineral in the Australasian seam (in the Sydney basin), where it occurs in association with kaolinite, quartz and montmorillonite–illite mixed layer minerals. This seam has been subjected to much volcanic activity which, it has been suggested, may have been responsible for the unusual predominance of montmorillonite. The presence of this mineral, although not reported in the younger coals from the Sydney basin which are the subject of the present study, should not cause any complications in the low-temperature oxidation. This matter is further discussed below.

X-Ray diffraction studies indicate that mica-type lattices and the crystalline lattice of kaolinite are generally stable at 380°C. This evidence, together with the data in the extensive literature on thermogravimetric and differential thermal analysis studies of hydrated silicate minerals (e.g. R. E. GRIM[11]; P. MURRAY and J. WHITE[12]; H. KIRSCH[13]), provide conclusive proof that the crystalline lattices of those minerals generally associated with coal are stable up to temperatures considerably in excess of 400°C. In some cases, notably kaolinite, a reversible loss of loosely bound water occurs below 400°C (Murray and White[12]). There appears to be some uncertainty regarding the thermal stability of the clay mineral illite. J. ENDELL[14] states that illite is stable up to temperatures in excess of 800°C, and Kirsch[13] puts the figure at 600°C, but according to Murray and White the water of constitution is evolved between 350° and 450°C. However, a consideration of dehydration–hydration data for illite, reviewed by Grim[11], indicates that most of the water evolved below 400°C is lost reversibly. With montmorillonite the irreversible loss of interlayer water below 400°C is only slight (Grim[11]; Murray and White[12]).

The carbonate minerals, calcite, ankerite and/or dolomite, have been identified by X-ray diffraction in the residues from prolonged oxidation at 380°C of various mine-dust and coal samples (Nagelschmidt[5]; Hicks and Nagelschmidt[6]). Differential thermal analysis (DTA) studies indicate the general thermal stability below 400°C of calcite, magnesite, dolomite, siderite and ankerite (e.g. J. L. KULP, P. KENT and P. F. KERR[15]; C. W. BECK[16]; R. A. ROWLAND and D. R. LEWIS[17]; H. W. VAN DER MAREL[18]). Siderite and magnesite appear to be the least stable, slow decomposition being first detected by DTA at 500° and 470°C respectively (Beck[16]). The thermodynamic data on metallic carbonates compiled by K. K. KELLEY and C. T. ANDERSON[19] are in general agreement with the DTA results with respect to calcium carbonate but indicate that ferrous carbonate (siderite) and, to a lesser extent, magnesium carbonate (magnesite), may decompose at lower temperatures; thus the dissociation (carbon dioxide) pressure was calculated to be 1 atmosphere at 187° and 369°C respectively for ferrous and magnesium carbonates. These decomposition pressures were calculated using thermodynamic data available at the time, and Kelley and Anderson[19] questioned the low value for ferrous carbonate. Further evidence for the thermal instability of ferrous carbonate is provided by the statement in the *Encyclopedia of Chemical Technology*[20] that the onset of decomposition occurs at 200°C and the dissociation vapour pressure reaches 1 atmosphere at 490°C. The present investigation (see below) confirmed that siderite is considerably less stable than DTA would indicate, in agreement with the thermodynamic calculations.

G.-M. SCHWAB and J. PHILINIS[21] showed that pyrite is readily oxidized in air at 400°C to form predominantly ferric oxide (a small amount of ferric sulphate is formed also). An exothermic peak at 400°C in the DTA curve for pyrite was interpreted as an indication of the formation of ferric oxide (Rowland and Lewis[17]). X-Ray diffraction studies indicate that pyrite is oxidized to ferric oxide (haematite) at 380°C (Nelson[7]).

On the basis of the foregoing evidence it seemed that at temperatures below 400°C the hydrated silicate minerals usually associated with coal could be

expected to lose reversibly only loosely bound water, whereas pyrite would be oxidized to ferric oxide, and siderite might undergo decomposition and oxidation to ferric oxide. A temperature of 370°C was selected for the low-temperature oxidation of coal in the present study.

In establishing the optimum experimental conditions for the low-temperature oxidation of coal for the purposes of isolating the mineral matter intact, or changed to a known extent, the precaution was adopted of holding the temperature near 200°C for two to three hours before raising it to 370°C. This reduces the total time required for the complete oxidation of the coal, probably because mild oxidation at 200°C prevents fusion and caking at 370°C (T. STADNICHENKO *et al.*[22]). The same procedure reduces the risk of establishing the exothermic luminescent oxidation (probably low-temperature ignition) that was observed to occur when some coal samples were heated rapidly to 380°C in air (J. D. BROOKS, private communication). Such occurrences could result in the minerals being subjected to temperatures considerably in excess of 380°C which would not be detected unless thermocouples were embedded in the sample.

Acid digestion (destructive) method

The details of the method used in the present investigation were as described by Radmacher and Mohrhauer[2] except that drying was carried out at 105° to 110°C in a vacuum oven and was followed immediately by weighing. This procedure proved to be more rapid and efficient than drying at 50°C and eliminated the need for subsequent moisture determination, provided that samples for the hydrochloric acid and ash determinations were weighed out immediately.

The assumption of Radmacher and Mohrhauer[2] that all the chlorine in the acid-treated coal is due to adsorbed hydrochloric acid introduces no significant error, since the total chlorine and hence organic chlorine content of Australian coals is generally very low. Also, since the residual ash in the acid-treated coals is usually very low, negligible error is introduced in the final estimate of the mineral matter by regarding this ash, less the ferric oxide (which is calculated to pyrite), as mineral matter. The possibility of formation of calcium fluoride during the acid treatment has been mentioned by W. RADMACHER and P. MOHRHAUER[23] and Bishop and Ward[4]; this point is discussed below.

KMC method

King, Maries and Crossley[1] based their mineral-matter formula on: (*i*) a consideration of the available analyses for clays associated with British coal deposits and for British ankerites, from which an average value for the water of constitution of the clay minerals and for the composition of the ankerites was derived; (*ii*) a consideration of the changes that occur in the minerals associated with British coals during ashing, namely loss of water of constitution of the clay minerals, oxidation of pyrites to ferric oxide, loss of carbon dioxide by carbonates, fixing of organic sulphur by lime (formed in the decomposition of calcite) in the ash, and decomposition of chlorides. The well known formula thus derived is:

Mineral matter = 1·09 Ash + 0·5 Pyritic sulphur + 0·8 Carbon dioxide + 2·5 Sulphate sulphur − 2·75 Sulphur in ash + 0·5 Chlorine

all analyses being expressed as percentage of air-dried coal.

Two recent publications amply illustrate the limitations of the KMC formula. J. O'N. MILLOT[24] has reinvestigated the water of constitution of the hydrated silicate minerals associated with British coals and found a variation over the range 8·1 to 14·6 per cent, with an average of 11·2 per cent. This value corresponds to an ash correction factor of 1·13, compared with a factor of 1·09 in the original KMC formula. W. J. S. PRINGLE and E. BRADBURN[25] have re-examined the composition of the carbonate minerals associated with British coals and obtained carbonate correction factors which vary over the range 0·58 to 0·97, the average of 0·8 being in agreement with the original KMC factor.

In the present study the mineral matter was calculated with this formula using both the original factor of 1·09 and the more recent factor of 1·13 (Millot[24]). With the latter factor the KMC formula becomes:

Mineral matter = 1·13 Ash + 0·46 Pyritic sulphur + 0·79 Carbon dioxide + 2·83 Sulphate sulphur − 2·83 Sulphur in ash + 0·5 Chlorine

EXPERIMENTAL

Full experimental details for both the low-temperature oxidation and the acid digestion methods are given in the Appendix.

For the purposes of the present study 24 coal samples were selected to test the two direct methods under a wide range of conditions, with particular reference to the presence of carbonates and pyrite. All samples were seam composites (excluding dirt bands), these being considered preferable to carefully isolated vitrain or float samples since the aim was to maintain high mineral-matter contents and thus test the direct methods under as severe conditions as possible. Representative analytical details for these coals are given in *Table 1*.

All mineral-matter-content determinations were made in duplicate for both direct methods.

Table 1. Representative analytical data for coals used in the investigation

Sample Nos.	*Seam*	*% Dry ash-free basis*		
		Carbon	*Hydrogen*	*Volatile matter*
1–10	*Bulli*	87·1	4·9	24·9
11–17	*Great Northern*	82·3	5·1	35·0
18–24	*Greta*	81·7	6·1	47·4

RESULTS AND DISCUSSION

Tables 2 and *3* respectively record the mineral-matter contents of the test coal samples as given by the low-temperature oxidation method and the acid digestion method. These results, together with those given by the KMC formula, are compared in *Table 4*.

Coals from the Bulli and Great Northern seams

The agreement between duplicates for each method and between the estimates of the mineral-matter contents obtained with the low-temperature oxidation and acid digestion methods was very good for coals from the Bulli and Great Northern seams. In the few cases where a significant difference was first obtained between methods (i.e. low values for the low-temperature oxidation method) it was noted that the carbonate carbon dioxide contents of the coals were high, although all high carbonate coals did not give this effect. It indicated the presence of some low-stability carbonate, and siderite was suspected (see above). Petrographic examination confirmed that siderite was in fact the predominant carbonate mineral in all but one of the troublesome samples, the exception being Sample 2 (*Table 2*). It was also confirmed that siderite nodules, hand-picked from a coal sample, lost carbon dioxide

Table 2. Mineral-matter determinations by low-temperature oxidation method
(All percentages are expressed on a dry-coal basis)

Sample No.	*Predominant carbonate mineral*	*M.M. (uncorrected)*		*Pyrite correction*	CO_2 *(coal)*	$FeCO_3$ *correction*		*M.M. (corrected)*	
		Duplicates	*Av.*			(a)	(b)	(a)	(b)
1	*Siderite*	12·71 12·67	12·69	0·03	1·13	0·26	0·51	12·95	13·23
2	*Ankerite*	14·87 14·97	14·92	0·05	2·52	0·57	0·66	15·54	15·63
3	*Siderite*	14·27 14·37	14·32	0·00	0·63	0·43	0·38	14·75	14·70
4	*Siderite*	11·95 12·08	12·02	0·10	0·96	0·33	0·52	12·35	12·64
5	*Ankerite*	13·47 13·55	13·51	0·00	0·67	*N.D.*	0·17	13·51	13·68
6	*Ankerite*	10·53 10·59	10·56	0·03	0·14	*N.D.*	0·08	10·59	10·67
7	*Siderite*	14·54 14·48	14·51	0·06	2·02	0·95	1·03	15·46	15·60
8	*Siderite*	12·63 12·52	12·58	0·04	1·01	0·29	0·52	12·87	13·14
9	*Ankerite*	11·58 11·60	11·59	0·10	0·16	*N.D.*	0·03	11·69	11·72
10	*Ankerite*	13·18 13·16	13·17	0·04	0·23	*N.D.*	0·13	13·21	13·34
11	*Siderite*	17·07 16·96	17·02	0·06	0·47	0·07	0·33	17·09	17·41
12	*Siderite*	17·97 17·89	17·93	0·04	0·74	0·29	0·57	18·22	18·54
13	—	19·45 19·45	19·45	0·06	0·03	*N.D.*	0·17	19·51	19·68
14	*Ankerite*	19·10 18·98	19·04	0·08	0·27	*N.D.*	0·19	19·12	19·31
15	*Ankerite*	15·63 15·64	15·64	0·00	0·75	*N.D.*	0·16	15·64	15·80
16	*Calcite*	15·45 15·43	15·44	0·03	0·79	*N.D.*	0·10	15·47	15·51
17	—	20·69 20·67	20·68	0·04	0·12	*N.D.*	0·16	20·72	20·88
18	*None found*	12·46 12·44	12·45	0·34	0·08	*N.D.*		12·79	
19	*Calcite*	13·37 13·33	13·35	0·45	0·17	*N.D.*		13·80	
20	*Calcite or ankerite*	14·28 14·28	14·28	0·08	1·20	*N.D.*		14·36	
21	*None found*	6·57 6·57	6·57	0·06	0·26	*N.D.*		6·63	
22	*Ankerite*	8·87 8·87	8·87	0·01	0·19	*N.D.*		8·88	
23	*Ankerite*	5·65 5·61	5·63	0·11	0·14	*N.D.*		5·74	
24	*Calcite*	7·48 7·57	7·53	0·23	0·22	*N.D.*		7·76	

Pyrite correction = 0·625 × pyritic sulphur.
N.D. = Not determined.
$FeCO_3$ correction: (*a*) = 0·82 (CO_2 coal − CO_2 low-temp. ash).
(*b*) = 0·645 (non-pyritic iron − ferrous iron equiv. of sulphate S).

equivalent to the iron content of the sample when heated under the conditions of low-temperature oxidation at 370°C, with the formation of ferric oxide. When a correction was applied to the low-temperature oxidation results assuming the difference in carbon dioxide contents (on a coal basis) of the coal and the mineral residue to be due to decomposition of siderite, very satisfactory agreement was again obtained with the results from the acid digestion method in all cases.

The behaviour of Sample 2 during low-temperature oxidation provides strong evidence that ferrous carbonate, irrespective of whether it is siderite or forms part of the mixed carbonate–ankerite lattice, decomposes at 370°C. This sample is very rich in carbonate mineral (*Table 2*), which was shown by both petrographic and chemical examination to be predominantly ankerite. For Sample 2 the mineral-matter content determined by low-temperature oxidation is in good agreement with the result given by the acid digestion method when the former is corrected by either

(*a*) attributing the decrease in carbon dioxide content (coal basis) during low-temperature oxidation to the decomposition of ferrous carbonate; or

(*b*) attributing the non-pyritic iron, less the iron equivalent of the sulphate content, to ferrous carbonate which has decomposed.

In fact, good agreement with the results given by the latter method is still obtained in all cases if this correction based on the iron is applied (*Tables 2* and *4*), although there is evidence that the procedure may involve a slight over-correction (Samples 1, 4, 8, 11 and 12 in *Table 2*).

With the acid digestion method a rough correlation was observed between the calcium content of the original coal and the amount of residual ash in the acid-treated coal. Bishop and Ward[4] made a similar observation on the effects of the acid digestion, using the carbonate carbon dioxide content as a guide to the calcium content. These authors attributed the phenomenon to the reaction of the hydrogen fluoride with calcium carbonate to form insoluble calcium fluoride, and recommended a preliminary hydrochloric acid treatment to remove the calcium carbonate for all coals containing more than 0·5 per cent carbonate carbon dioxide. In the present investigation an initial hydrochloric acid treatment of some selected samples caused a considerable reduction in the residual ash [compare *Tables 3*(a) and *3*(b)]. Bishop and Ward assumed that the calcium fluoride in the acid-treated coal is converted to calcium oxide on ashing, with the result that a low estimate is obtained for the mineral-matter content. However, available evidence suggests that calcium fluoride is stable at the ashing temperature—for example, during the gravimetric determination of fluorine as calcium fluoride the final precipitate is ignited at 800° to 900°C to constant weight (W. F. HILLEBRAND *et al.*[26]). The formation of calcium fluoride during the acid digestion would not affect the mineral-matter determination if the calcium fluoride remained unchanged in the residual ash. *Table 3*(b) shows that a preliminary hydrochloric acid treatment caused an increase in the estimated mineral-matter content in only one instance (Sample 2).

Table 3. Mineral-matter determinations by acid digestion method.
(a) Without pretreatment
(All percentages are expressed on a dry-coal basis)

Sample No.	CaO %	*Loss in wt %*	*Adsorbed* HCl %	*Pyrite %*	*Residual ash %*	*Dry M.M. %*	
						Duplicates	*Av.*
1	0·42	12·00 11·97	0·67 0·67	0·08 0·09	0·44 0·34	13·19 13·07	13·13
2	1·60	11·50 12·05	0·74 0·69	0·14 0·17	2·54 2·14	14·92 15·05	14·99
3	0·22	13·75 13·72	0·81 0·69	0·20 0·09	0·29 0·26	15·05 14·76	14·91
4	0·39	11·24 11·21	0·76 0·69	0·14 0·11	0·45 0·44	12·59 12·45	12·52
5	0·53	12·05 12·41	0·71 0·69	0·08 0·07	0·62 0·46	13·46 13·63	13·54
6	0·06	9·45 9·63	0·77 0·80	0·04 0·04	0·18 0·19	10·44 10·66	10·55
7	0·62	13·80 14·10	0·73 0·72	0·12 0·12	0·74 0·59	15·39 15·53	15·46
8	0·38	11·66 11·76	0·75 0·78	0·15 0·13	0·42 0·40	12·98 13·07	13·03
9	0·25	10·53 10·53	0·77 0·76	0·18 0·18	0·29 0·31	11·77 11·78	11·78
10	0·19	12·36 12·29	0·68 0·68	0·11 0·12	0·24 0·19	13·39 13·28	13·34
11	0·05	15·95 15·90	1·01 0·94	0·18 0·24	0·17 0·16	17·31 17·24	17·28
12	0·06	16·95 16·91	0·93 0·93	0·16 0·20	0·16 0·18	18·20 18·22	18·21
13	0·10	18·11 18·11	0·92 0·95	0·12 0·16	0·18 0·16	19·33 19·38	19·36
14	0·15	17·53 17·55	0·92 0·94	0·24 0·27	0·26 0·25	18·95 19·01	18·98
15	0·86	13·44 13·55	1·06 1·02	0·13 0·14	0·93 0·92	15·56 15·63	15·60
16	0·78	13·39 13·29	0·99 1·04	0·13 0·14	0·81 0·85	15·32 15·32	15·32
17	0·21	19·29 19·26	0·91 0·99	0·12 0·12	0·25 0·24	20·57 20·61	20·59
18	0·43	10·28 10·42	1·12 1·00	0·97 1·00	0·58 0·50	12·95 12·92	12·94
19	0·57	9·93 9·91	1·10 0·97	1·61 1·57	0·98 0·97	13·62 13·42	13·52
20	2·58	7·78 7·96	0·78 0·66	0·28 0·26	5·14 4·71	13·98 13·59	13·79
21	0·27	4·68 4·81	1·48 1·43	0·26 0·26	0·50 0·49	6·92 6·99	6·96
22	0·14	7·36 7·28	1·20 1·32	0·26 0·26	0·36 0·32	9·18 9·18	9·18
23	0·25	4·12 4·15	1·26 1·32	0·49 0·46	0·44 0·42	6·32 6·35	6·34
24	0·26	5·23 5·48	1·26 1·22	0·70 0·65	0·62 0·59	7·81 7·94	7·88

[*continued opposite*

Table 3—continued
(b) With initial hydrochloric acid treatment

Sample No.	CaO %	*Loss in wt %*	*Adsorbed* HCl %	*Pyrite %*	*Residual ash %*	*Dry mineral matter %*		
						Dupl.	*Av.*	*Without initial* HCl
2	1·60	14·18 13·90	0·76 0·67	0·08 0·09	0·46 0·68	15·48 15·34	15·41	14·99
5	0·53	12·68 12·68	0·73 0·67	0·06 0·06	0·15 0·14	13·62 13·55	13·59	13·54
7	0·62	14·45 14·50	0·73 0·67	0·08 0·07	0·15 0·09	15·41 15·33	15·37	15·46
15	0·86	14·11 14·07	1·18 1·16	0·10 0·10	0·23 0·22	15·63 15·55	15·59	15·60
16	0·78	14·11 14·03	1·07 1·05	0·11 0·11	0·13 0·17	15·42 15·36	15·39	15·32
20	2·58	9·33 9·79	0·70 0·73	0·22 0·22	3·16 2·76	13·41 13·50	13·46	13·79

The negligible change in the total mineral-matter estimate for the rest of the samples (from the Bulli and Great Northern seams) when considered together with the significant decrease in the residual ash in the acid-treated coal due to pretreatment with hydrochloric acid, tends to confirm the formation and thermal stability of calcium fluoride. To account for the behaviour of Sample 2, some evidence has been obtained which suggests that the high residual ash may in fact be due to the non-digestion of calcium carbonate through the formation of a protective coating of insoluble calcium fluoride. This effect would be expected to be variable, because of its dependence on the size and distribution of calcium carbonate in the coal.

The good agreement between the results with the two methods, which are directly opposed in their approach, is regarded as ample evidence that both are reliable and that under the conditions of the low-temperature oxidation method there was no unsuspected decomposition of minerals, with the possible exception of ankerite. Also the overall agreement between the two direct methods is much better than the general agreement between the results obtained with either of them and those calculated using the KMC formula, irrespective of whether the original ash correction factor of 1·09 or the revised (Millot[24]) value of 1·13 was used. Adopting the latter alternative, the calculated values were always higher than those obtained by direct estimation, whereas using the 1·09 ash correction factor the calculated values showed no consistent bias, being sometimes very close to, sometimes lower, and sometimes higher, than the direct estimates. This behaviour of the KMC results is as would be expected when the constitution of the minerals (particularly with respect to water of hydration) differs from the assumed 'average' constitution and varies from sample to sample. It would appear that for the mineral matter in coals from the Bulli and Great Northern seams the factor 1·09 is preferable.

Coals from the Greta seam

Some complications were experienced with coals from the Greta seam. Good agreement was obtained for two of the seven samples studied, while the low-temperature oxidation result was lower than the acid digestion results

Table 4. Comparison of mineral-matter estimates from acid digestion, low-temperature oxidation, and KMC methods*

Sample No.	*Low-temperature oxidation†* %		*Acid digestion method* %	*KMC* (i) %	*KMC* (ii) %	*Ash* (775°C) %
	(a)	(b)				
1	13·0	13·2	13·1	13·1	13·5	11·4
2	15·5	15·6	15·0 (15·4‡)	15·3	15·8	12·5
3	14·8	14·7	14·9	14·5	15·0	12·8
4	12·4	12·6	12·5	12·6	13·0	10·9
5	13·5	13·7	13·6 (13·6‡)	13·2	13·7	11·9
6	10·6	10·7	10·6	10·5	10·9	9·6
7	15·5	15·6	15·5 (15·4‡)	15·7	16·2	13·2
8	12·9	13·1	13·0	13·0	13·4	11·3
9	11·7	11·7	11·8	11·6	12·0	10·4
10	13·2	13·3	13·3	13·1	13·5	11·8
11	17·1	17·4	17·3	17·2	17·8	15·4
12	18·2	18·5	18·2	18·4	19·1	16·4
13	19·5	19·7	19·4	20·1	20·8	18·4
14	19·1	19·3	19·0	19·2	19·8	17·4
15	15·6	15·8	15·6 (15·6‡)	15·3	15·8	13·6
16	15·5	15·6	15·3 (15·4‡)	15·1	15·6	13·4
17	20·7	20·9	20·6	20·9	21·7	19·1
18	12·8	—	12·9	12·3	13·0	8·2
19	13·8	—	13·5	12·6	13·4	7·8
20	14·4	—	13·8 (13·5‡)	12·9	13·4	11·8
21	6·6	—	7·0	6·7	7·0	5·9
22	8·9	—	9·2	8·9	9·2	7·9
23	5·7	—	6·3	5·8	6·0	4·4
24	7·8	—	7·9	7·5	7·8	6·2

* All percentages are on a dry-coal basis, and all mineral-matter estimates are rounded off to the first decimal place, to facilitate comparison.

† (*a*) Ferrous carbonate correction, CO_2 basis.
(*b*) Ferrous carbonate correction, Fe basis.

‡ Preliminary HCl treatment.

(*i*) M.M. = $1{\cdot}09\,A + 0{\cdot}5\,S_{pyr} + 0{\cdot}8\,CO_2 + 2{\cdot}5\,S_{SO_4} + 0{\cdot}5\,Cl - 2{\cdot}75\,S_{ash}$

(*ii*) M.M. = $1{\cdot}13\,A + 0{\cdot}46\,S_{pyr} + 0{\cdot}79\,CO_2 + 2{\cdot}83\,S_{SO_4} + 0{\cdot}5\,Cl - 2{\cdot}83\,S_{ash}$

where A = ash (per cent); S_{pyr} = pyritic sulphur (per cent); S_{SO_4} = sulphate sulphur (per cent); CO_2 = carbon dioxide (per cent); Cl = chlorine (per cent); S_{ash} = sulphur in ash (per cent); all expressed as percentages of air-dried coal.

for three samples and higher for the remaining two. Duplicate determinations for each method of analysis agreed very well in all cases. The Greta coals were selected primarily in order to try out both methods on coals containing a high percentage of pyrite. Unfortunately, however, the test samples had been stored for a considerable period prior to the experiments, and these

showed that as a result a major proportion of the pyrite had in all cases become oxidized, with some loss in total sulphur content and a considerable increase in sulphate content (*Table 5*). It was found that this sulphate was predominantly ferrous, although there had been some formation of calcium, magnesium and sodium sulphate, due, presumably, to attack by sulphuric acid, formed during the aerial oxidation of the pyrite (H. F. COWARD[27]), on other minerals present.

Table 5. Effect of storage on pyritic-sulphur content of coals from the Greta seam

Sample No. / Sampling date		18 Oct 51	19 Nov 51	20 Feb 52	21 Jun 53	22 Aug 53	23 Sep 53	24 Aug 55
% Ash	orig.	8·46	8·03	11·26	6·03	7·92	4·31	6·18
	recent*	8·22	7·82	11·82	5·86	7·88	4·40	6·18
% Pyritic sulphur	orig.	2·24	3·05	0·41	0·13	0·20	0·73	0·63
	recent*	0·56	0·75	0·13	0·10	0·02	0·18	0·38
% Sulphate sulphur	orig.	0·03	0·04	0·03	*Trace*	*Trace*	0·03	0·01
	recent*	1·30	1·66	0·25	0·10	0·09	0·39	0·27
% Carbon dioxide	orig.	0·15	0·37	1·28	0·22	0·26	0·30	0·22
	recent*	0·08	0·17	1·20	0·26	0·19	0·14	0·22

* 'Recent' analyses made in March 1958.

Although there seems no doubt that the oxidation products of pyrite caused the complications observed, the lack of fundamental data on the mechanism of pyrite decomposition and oxidation during storage, and in the presence of other minerals, makes it difficult to offer a satisfactory explanation of the observed effects. The degree of hydration of the ferrous sulphate and other sulphates formed, and the thermal stability of these hydrates, are not known. To further complicate the picture, the observed effects do not vary with the sulphate content of the coals, although the degree of moisture pick-up during the re-equilibration stage of the low-temperature oxidation method varied with the sulphate content; nor is there any correlation with the pyritic sulphur content.

The two Greta coals (Samples 19 and 20) for which the low-temperature oxidation yielded high results happen to be those richest in calcium (*Table 3*).

The acid-treated Sample 20 had a high residual ash content which was only partially reduced by a preliminary hydrochloric acid treatment, indicating that most of the residual ash was not calcium fluoride or 'protected' calcium carbonate (see above). The preliminary pretreatment also gave a reduction in the determined amount of mineral matter [*Table 3*(b)]; the reason for this is obscure.

For the Greta coals no attempt was made to apply a correction to the low-temperature oxidation results for the decomposition of ferrous carbonate, since high sulphate sulphur (*Table 5*) in these weathered coals is not all ferrous sulphate. Such a correction would be small since the carbonate content is low in all but one sample from this seam.

No complications were observed due to the pyritic sulphur content of coals from the Bulli and the Great Northern seams.

CONCLUSIONS

Both the low-temperature oxidation and the acid digestion methods for the direct determination of the quantity of mineral matter present in coal are capable of giving reliable results.

With the low-temperature oxidation method the time required for the complete oxidation of the coal substance is not a disadvantage, since several samples can be processed simultaneously and virtually no attention is required once the final temperature has been set. Corrections are required for the decomposition of ferrous carbonate and for the oxidation of pyrite during the low-temperature oxidation procedure, if these compounds are present to an appreciable extent. Coals rich in pyritic sulphur may cause trouble if the pyrite has undergone aerial oxidation. The low-temperature oxidation method is readily adaptable to routine determinations and provides a supply of mineral matter for more detailed investigations.

The acid digestion method requires more skill, more operator time, and more analytical work than the low-temperature oxidation method, besides involving the undesirable use of hydrofluoric acid.

The King–Maries–Crossley formula in either the original or the modified form (Millot[24]) cannot be relied upon to yield precise estimates of the mineral-matter content in Australian coals.

Thanks are due to Dr G. H. Taylor for petrographic data and to M. S. Burns for analytical data on the coals used in this investigation.

The work was carried out as part of a programme of investigation by the Coal Research Section into the nature and behaviour of the inorganic constituents in Australian coals.

Coal Research Section,
Commonwealth Scientific and Industrial
Research Organization, P.O. Box 3,
Chatswood, New South Wales, Australia (*Received October 1958*)

APPENDIX

Experimental details of low-temperature oxidation method

One gramme of coal sample was weighed into a silica dish and then placed in a well ventilated furnace (Ockleford low-temperature type). The temperature was raised to about 200°C and held constant for 2 to 3 hours. It was then raised to, and maintained at, 370° ± 10°C until the sample was oxidized to constant weight (about 100 hours was required to complete the oxidation of the coals tested). After removal from the furnace the mineral residue was cooled and then equilibrated with moisture at 100 per cent relative humidity at room temperature, by placing in a closed vessel over water, in order to restore the reversible loss by the clay minerals of loosely bound water (Murray and White[12])*. The sample was then dried at 105° to 110°C for 1 hour and the silica dish weighed immediately with and without the residual mineral matter. The mineral-matter content of the coal was calculated as follows:

$$\text{Percentage of mineral matter} = 100\, W_m/W + 0{\cdot}625\ \text{Pyritic sulphur} + 0{\cdot}82\ \Delta\ CO_2$$

or, alternatively†,

* Pick-up of moisture (dry basis, 105° to 110°C) was always less than 1 mg, corresponding to less than 0·1 per cent of the mineral matter (except for Greta coals, whose pick-up was high).
† This procedure is the easier to use since it requires no analytical work beyond the usual sulphur determinations.

Percentage of mineral matter = 100 W_m/W + 0·625 Pyritic sulphur + 0·645 Δ Fe

where W_m = weight of mineral residue (dry basis, 105° to 110°C); W = weight of original coal sample (dry basis, 105° to 110°C); 0·625 Pyritic sulphur = correction for loss in weight due to conversion of all the pyrite to ferric oxide (percentage of pyritic sulphur expressed on dry-coal basis); Δ CO_2 = the difference in the percentage carbon dioxide in the original coal sample and in the mineral residue, both expressed on dry original-coal basis (0·82 Δ CO_2 is the correction for the weight change due to decomposition of ferrous carbonate to ferric oxide), and Δ Fe = non-pyritic iron less ferrous iron equivalent of sulphate content, expressed as percentages on dry-coal basis (0·645 Δ Fe is the correction for the weight change due to decomposition of ferrous carbonate assuming that all the sulphate is present as ferrous sulphate).

*Experimental details of acid digestion method**

A known weight of coal (5 to 6 g) at minus 72 B.S. mesh was treated with 40 ml of 40 per cent hydrofluoric acid at 50°C for 45 minutes in a plastic beaker. The hydrofluoric acid was then decanted off through a specially designed Buchner-type filter funnel fabricated from a single piece of Teflon (*Figure 1*) and fitted with Whatman No. 50 filter paper. Any coal

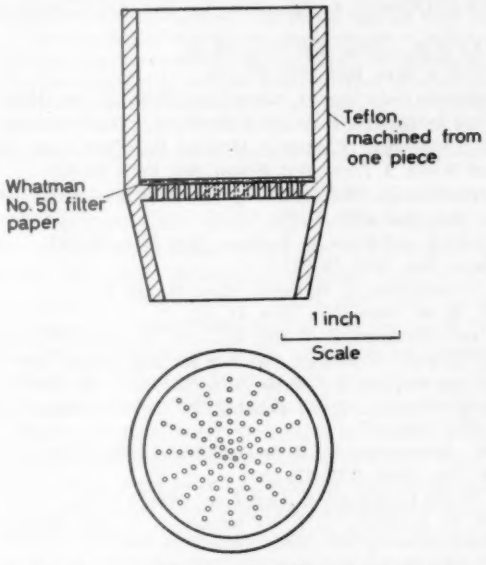

Figure 1. Teflon filter for the acid digestion procedure

transferred to the filter during this step was returned to the bulk of the coal in the beaker, and this coal was then treated with 50 ml of concentrated hydrochloric acid (approximately 10N) at 50°C for a further 45 minutes. The coal was filtered off and washed thoroughly with 500 ml of hot (approximately 80°C) distilled water. The filter containing the treated coal was dried at 105° to 110°C in a vacuum oven for 2 hours. The filter plus dried coal was weighed and the filter reweighed after removal of the coal, the difference representing the

* If a high calcium content is suspected (i.e. more than about 1 per cent CaO on dry-coal basis) an initial hydrochloric acid treatment (5N) is advisable to prevent complications due to the formation of calcium fluoride. Bishop and Ward[4] advocate this procedure if the carbonate carbon dioxide content exceeds 0·5 per cent; although this should include all coals likely to cause trouble the present authors have found that the calcium content is a more reliable guide.

weight of the residual (acid-treated) coal. This residual coal was then analysed for ash, chlorine (assumed present as hydrogen chloride) and ferric oxide (assumed all derived from the pyrite in the original coal). The mineral-matter content of the original coal was calculated as follows:

$$\text{Percentage mineral matter} = \{(W_1 - W_2 + P + \text{HCl} + A)/W_1\} \times 100$$

where W_1 = weight of original coal (dry basis, 105° to 110°C); W_2 = weight of treated coal (dry basis, 105° to 110°C); P = weight of pyrite in the original coal, calculated from the ferric oxide content of the ash of the acid-treated coal; HCl = weight of hydrogen chloride in the acid-treated coal; and A = weight of ash in the acid-treated coal less the ferric oxide in the ash.

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Electron Resonance Study of the Free Radicals produced by Electrolysis of Solvent Extracts of a Coal

D. E. G. AUSTEN, P. H. GIVEN, D. J. E. INGRAM and M. E. PEOVER

It has previously been shown by electron resonance measurements on samples withdrawn and frozen at −180°C that free-radical-ions are produced when certain aromatic substances of known structure are reduced electrolytically in dimethylformamide at a controlled potential slightly more negative than the respective half-wave potentials. Similar measurements show that in the electrolysis of solvent extracts of a coal, the radicals originally present are rapidly reduced, and then the radical concentration increases as fresh radicals are produced by the electrolysis. It is suggested that the observed production of radicals when extracts are reduced at −2·2 V indicates the presence of naphthalene, phenanthrene or diphenyl ring systems. In contrast to the free-radical-ions produced by the electrolysis of anthracene or benzophenone, those resulting from the reduction of coal are stable at room temperature. This stability is shown to result from a low rate of proton addition and thus the observation is in line with an earlier conclusion that coals show a resistance to the addition of hydrogen.

POLAROGRAPHIC reduction in a non-proton-releasing solvent consists essentially of electron addition. One would expect free radicals, containing unpaired electrons, to be readily reduced to a stable non-paramagnetic product. Stable free radicals have been detected in coals (2 to 25 × 10^{18} radicals/g)[1]: the colour and electrical properties of coals may owe something to their presence. It was suggested[2] that these stable radicals could be characterized by determining the minimum potential required in controlled potential electrolysis to reduce the initial electron resonance signal to zero. The electron affinity of radicals measured in this way should be a clue to their nature. In an attempt to test this suggestion, solvent extracts of various coals were reduced electrolytically at controlled potentials between −1 and −2·2 V in dimethylformamide, the products were isolated from the solutions, and their electron resonance signals determined. It was observed that even at −2·2 V the decrease in the signal was not large, and that in some cases at less negative potentials the signal given by the reduced product was actually greater than that of the starting material. It was these observations that prompted the present investigation, whose object was therefore to ascertain how the concentration of free radicals varied during the course of the electrolytic reduction of some solvent extracts of a coal. A parallel investigation of the production of radicals during the electrolytic reduction of some substances of known structure has been reported elsewhere[3].

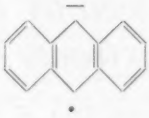
In a non-proton-releasing solvent there are three distinct stages in electrolytic reduction:

$$R + \varepsilon = R' \qquad \text{(a free-radical-ion)} \qquad \ldots . [1]$$

$$R' + \varepsilon = R'' \qquad \text{(an ion but not a radical)} \qquad \ldots . [2]$$

$$R' + 2H^+ = RH_2 \qquad \text{(a stable product)} \qquad \ldots . [3]$$

For example when R is anthracene, R′ has the structure



Reaction 2 normally takes place at a considerably more negative potential than reaction 1; and reaction 3 is slow and takes place by abstraction of protons from the solvent[4]. Previous results[5,6] suggest that both stages 1 and 2 should be complete for any quinone groups in coal extracts by about −1 V versus mercury pool anode, and both steps for aromatic systems by −2·2 V (the most negative potential obtainable in the medium used). At −1·5 to −1·6 V one would expect most of the aromatic systems in coal extracts to have completed step 1 only, thus becoming free-radical-ions. The free radical triphenylmethyl has a half-wave potential of about −0·62 V, at which its odd electron is paired[7]. These data guided the choice of experimental conditions and the interpretation of the results in the work to be described.

EXPERIMENTAL

The apparatus and methods for the electrolyses have been described previously[8]. The coal extracts were dissolved in 0·1N tetraethylammonium iodide in dimethylformamide, and reduction took place on a stirred mercury cathode. At intervals during the electrolyses small samples were withdrawn under oxygen-free nitrogen into tubes of a size to fit exactly the resonant cavity of the spectrometer. The tubes were in most cases immediately chilled in liquid nitrogen and sealed; the resonance signal was measured a few hours later, with the sample still at −180°C, in a 3 cm wavelength electron resonance spectrometer (for further details of the instrument and method of measurement see ref. 9). The absolute accuracy of the measurements of radical concentration in the sample tubes is estimated to be about ± 20 per cent. Two solvent extracts of one coal were studied: the dimethylformamide-soluble parts of a pyridine and an α-naphthol extract of coal DIX (86·2 per cent carbon). Both materials were made by Soxhlet extraction.

RESULTS

The results are presented in *Figures 1* and *2*. It will be noted that when the pyridine extract was reduced, one set of samples was collected and immediately frozen at −180°C, and intermediately another set was collected, kept at room temperature, and frozen at −180°C only at the time of measurement. In the second experiment with the α-naphthol extract, reduction was carried out at −1·6 V until the current had fallen to a fairly low value, four samples being collected in this period, and then phenol was added in the proportion 17·5 g/l.; other (unpublished) work had shown that phenol gives no reduction or hydrogen discharge waves itself, but is an effective proton-donor in the reduction of other substances. Two further samples were collected, and when the

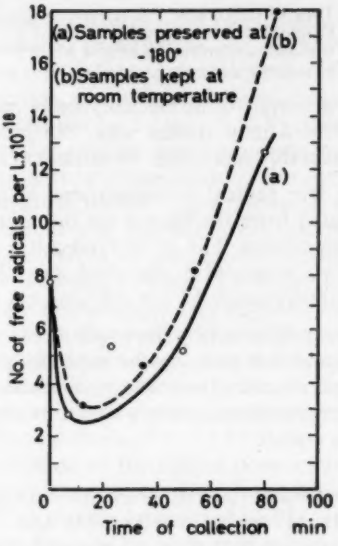


Figure 1. Production of free radicals from dimethylformamide-soluble part of pyridine extract of coal DIX; concentration 9·6 g/l.

current had again fallen to a low value, the potential was increased to −2·1 V, and a final sample was taken.

Some of the samples of α-naphthol extract reduced at −1·6 V were allowed to warm up to temperature after the resonance signals had been measured at −180°C. After 4 h at room temperature the signal was re-measured, with the results tabulated overleaf.

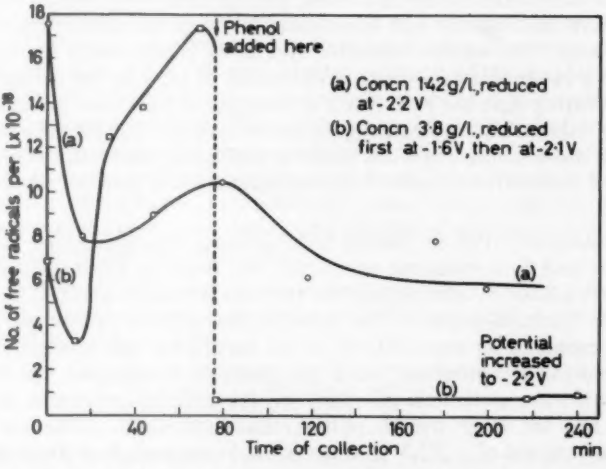


Figure 2. Production of free radicals from dimethylformamide-soluble part of α-naphthol extract of coal DIX

Time of collection	48	118	199	min
Original radical concentration	8·9	6·15	$5{\cdot}65 \times 10^{18}$	per litre
Radical concentration after 4 h	8·3	4·8	$3{\cdot}8 \times 10^{18}$	per litre
Fractional decrease	17	22	33	per cent

When a sample of an electrolytically reduced anthracene solution (see ref. 3) was treated in a similar way, the radical concentration was found to be immeasurably small after 10 minutes at room temperature.

The free radical concentrations in the original isolated extracts can be calculated from the figures for the solutions at zero time. The results were: pyridine extract, $0{\cdot}81 \times 10^{18}$ radicals/g (cf. an earlier preparation of the same material, measured in the solid state, $3{\cdot}3 \times 10^{18}$); the two preparations of α-naphthol extract, $12{\cdot}3 \times 10^{18}$ and $1{\cdot}8 \times 10^{18}$ radicals/g, respectively.

The signal given by the pyridine extract in solution had a line width of 13 gauss, and that given by the naphthol extract 11 gauss; these values were unchanged on reduction. The g values were $2{\cdot}002 \pm 0{\cdot}001$, which is identical within experimental error with the free-spin value.

DISCUSSION

The resonance signals given by different preparations of the same extract (unreduced) are not reproducible, and values calculated for the pure material from solution data do not agree with those measured directly. It is likely that radical sites are more accessible to reaction when the material is in solution, and a proportion of the radicals in the coal may be destroyed by reaction with solvent or adventitious impurities in it. Nevertheless the *changes* in radical concentration during the reduction of any one sample should be significant.

In all cases there was a sharp drop in free radical concentration at the beginning of the electrolysis. This must represent reduction of the radicals existing in the extracts before reduction, and the behaviour implies that these radicals have less negative half-wave potentials than the bulk of the material being reduced. The various reducible species of course reach the electrode surface in a random order—there is no reason to suppose the radicals more rapidly diffusing than the rest. But if a molecule of half-wave potential, say, −1·5 V is reduced and subsequently in the bulk of the solution encounters an unreduced molecule having a less negative half-wave potential, the latter will be reduced by electron transfer from the former (such transfer reactions are rapid[10,11]).

The subsequent rises in radical concentration resemble those found in anthracene and benzophenone solutions[3], and must be ascribed to the production of radicals by electrolysis. (In the coal solutions, about 0·1 to 1 per cent of the electrons added to the solute at the cathode are measurable by electron resonance as unpaired.) It is not surprising that in electrolysis at −1·6 V radicals are produced, since this potential lies between the first and second half-wave potentials of many of the simpler polycyclic aromatic systems. But the large rise in radical concentration in reduction of the α-naphthol extract of −2·2 V is unexpected. It suggests that there is in the extract an appreciable concentration of aromatic structures whose second reduction wave occurs at a potential more negative than −2·2 V; the available

information[7,12] shows that few aromatic structures—the most unreactive—can have this property. Of these structures, naphthalene and phenanthrene give in dimethylformamide only one wave of height equivalent to the addition of one electron[6], suggesting that there is a second wave beyond the decomposition potential of the supporting electrolyte (−2·2 to −2·30 V). However, both these substances in dioxan–water also give one wave[7] at nearly the same potential as in dimethylformamide, but of height equivalent to two electrons. It is possible that the wave in the anhydrous solvent really represents a two-electron charge, and the observed current was low for some unexplained reason; but it is more likely that there is indeed an inaccessible second wave in a solvent where the rate of proton addition is lower. Diphenyl and triphenylene also have their first half-wave potentials at very negative voltages in dioxan–water and cellosolve[7,11], so that they might give radical-ions at −2·1 to −2·2 V, but their polarography has not been studied in dimethylformamide. Therefore it may be said that the presence in the coal extract of naphthalene and phenanthrene (and also perhaps diphenyl and triphenylene) systems is indicated by the production of radicals of −2·2 V. However, it is theoretically possible that some contribution to the radical concentration is made by species having a third or fourth wave at potentials beyond −2·2 V; this situation could arise if a di-ion R'' is rapidly protonated to RH_2 and the latter is then reduced further, but is not likely to be important because rates of protonation are *not* rapid in dimethylformamide.

The similarity of the radical concentrations in the samples of the extracts kept at room temperatures to those in the samples preserved by freezing (see *Figure 1* and the results tabulated above) is striking, and is in marked contrast to the behaviour of anthracene and benzophenone. The extreme stability of the radical-ions from coals could be accounted for by supposing the rate of protonation to be very slow, so that further reduction to non-paramagnetic dinegative ions is not possible at the potential used. It has already been deduced[13] from other aspects of the behaviour of coal extracts on reduction that their structures are reluctant to add protons; this effect is most marked with low rank coals but is still appreciable in extracts of the coal DIX and has been associated[13] with resistance of the structures to the deformation brought about by hydrogen addition. This explanation of the stability of the free-radical-ions is confirmed by the large drop in radical concentration (accompanied by a rise in current during the electrolysis) when phenol is added as a proton-donor (see *Figure 2*). Incidentally, these conclusions imply that in order to secure the maximum degree of reduction of coal extracts by electrolysis, a proton-donor should be present.

The results in *Figure 1* may be contrasted with the following, which represent radical concentrations in the recovered solid products of reduction of a pyridine extract of coal DIX:

Unreduced extract, $3{\cdot}3 \times 10^{18}$ radicals/g
Reduced at −1·0 V, $4{\cdot}4 \times 10^{18}$
Reduced at −1·6 V, $3{\cdot}2 \times 10^{18}$
Reduced at −2·2 V, $1{\cdot}7 \times 10^{18}$

These data show that some of the radicals produced by electrolysis are not merely not protonated and reduced further in the course of the experiment, but survive the addition of water and the recovery procedure.

Other similar sets of data have been obtained with extracts of other coals. This surprising result cannot be accounted for at present.

Three points arise from this work that seem to merit further study. First, a study of the electrolysis of naphthalene, phenanthrene, diphenyl and perhaps triphenylene by the methods used here should show whether the suggestion that the coal extract contains these systems is sound. Second, information about the ease of proton addition to extracts of coals of different ranks would be useful (it should be noted that although the free radicals pre-existing in coals represent only a small fraction of the whole structure, those produced by electrolysis are characteristic of a major part since every molecule that is reduced must pass through a radical stage in the course of reduction). Third, determination of the potential at which the initial drop in radical concentration disappears should give an indication of the electron affinity of the pre-existing radicals and hence provide a clue to their nature.

The electrolyses were carried out in the Chemisty Department of the British Coal Utilisation Research Association and the work is published by permission of the Association. The electron resonance measurements were made in the Department of Electronics, University of Southampton.

British Coal Utilisation Research Association, Randalls Road, Leatherhead, Surrey

Department of Electronics, University of Southampton

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Analysis of Liquid Products from Coal Hydrogenation by Mass Spectrometry

Use of Rhenium Filaments and Low Ionizing Voltage

A. G. SHARKEY, Jr, G. WOOD, JANET L. SHULTZ, I. WENDER and R. A. FRIEDEL

A combination of data obtained with low ionizing voltage and with conventional type-analysis permits rapid comparisons of coal hydrogenation products. Molecular weights and structural types can be determined in the aromatic and saturated fractions. Type-analysis methods that are relatively independent of structural variations have been applied to these two fractions. Many structural types in the phenolic portion can be identified from two mass spectrometer runs, one on the original sample, the second on the trimethylsilylether derivative. A limited number of spectra of pure phenol derivatives, made at low ionizing voltage, indicate that a semiquantitative determination of carbon number distribution in phenolic fractions based on relative peak intensities is valid. Rhenium filaments offer much better temperature and pattern stability, particularly for analysing samples containing large percentages of aromatics.

ANALYSIS of high boiling tar acids from petroleum, coal, and neutral oils from coal has consisted largely of the laborious isolation of individual pure compounds. The procedures usually involve chemical treatment of the oil and provide only an approximation of the amount of certain compounds present in the original oil.

Routine mass spectrometric analysis of liquid products from coal hydrogenation has been limited primarily to the determination of certain hydrocarbon types[1]. We normally determine total paraffins, total naphthenes, C_6 to C_{10} alkyl benzenes, tetralin, and naphthalene in fractions boiling up to 200°C. Little information can be deduced from spectra of such mixtures as to molecular weights or types of compounds represented in the very non-specific spectra of higher boiling fractions. Adjacent mass peaks have approximately the same intensities, seldom varying by a factor greater than two. These non-distinct spectra result from the presence of many compounds having similar spectra and from rearrangement ions corresponding to the molecular weights of lower members of homologous series.

In repeated analyses of samples containing large percentages of aromatic compounds, tungsten emitters exhibit gas-sensitivity, that is, behaviour of the instrument depends on the nature of the gases introduced previously. The temperature of the ion source is not constant and spectral patterns are not stable. Rhenium filaments were substituted in the ion sources in an attempt to overcome these difficulties.

INSTRUMENTATION

Two type 21–103 Consolidated Mass Spectrometers were used, the first with an inlet system operating at room temperature, the second with a heated system operable up to 350°C.

Rhenium emitters were used in this investigation and have been used in analytical mass spectrometers in this laboratory for over a year[2,3]. Many properties of rhenium and its possible applications in electronics had been investigated by C. T. SIMS[4], and by E. WYLER, D. GIDEON and F. TODD[5]. Several of these properties make rhenium a desirable electron emitter. It melts at approximately 3180°C only 232° below tungsten. Its thermionic work function is 4·80 V, compared with 4·56 for tungsten. Rhenium is considerably more resistant than tungsten to the water cycle, a major advantage in mass spectrometry as many samples contain large percentages of water. Further, rhenium remains ductile at all temperatures and therefore is less likely to be ruptured by thermal or mechanical shock. It is easily spot welded. Its carbides are unstable. One may expect the service life of a rhenium emitter to be comparable to that of a tungsten emitter in an analytical mass spectrometer.

The tungsten wire on a standard filament assembly for a Consolidated type 21–103 mass spectrometer was replaced with a rhenium wire of the same diameter (0·007 in.). Both rhenium and tungsten heaters have been used on assemblies having rhenium filaments. Satisfactory operation was obtained, and the temperature of the ion source could be controlled at the usual 250°C. For the same emission, rhenium filaments required less current than tungsten filaments, 3·0 instead of 3·8 A. Data showing a comparison of *n*-hexadecane patterns obtained with rhenium and tungsten filaments are given in *Table 1*.

Table 1. Comparison of mass spectral patterns with rhenium and tungsten filaments—three weeks period with each filament

m/e	*Average patterns for* n-*hexadecane*	
	Rhenium	*Tungsten*
	%	%
226	100	100
197	17·4	17·7
183	30·1	30·8
169	45·7	46·0
155	56·3	57·3
127	79·4	81·6
Average deviation from average for mass 127, three weeks period	0·78	2·2

These data indicate a factor of three decrease in the average deviation for the rhenium filaments. With the rhenium filament in use, only minor adjustments were required in the ion source heater every three or four days. Continual adjustment, many times with each aromatic sample introduction, was required with the tungsten filament to maintain constant ion source temperature.

Rhenium filaments in the heated-inlet mass spectrometer were exposed for several months to the same variety of high-molecular-weight aromatic compounds that caused difficulty with tungsten filaments. Operation was satisfactory at all times without evidence of gas sensitivity.

ANALYSIS OF NEUTRAL AND TAR ACID FRACTIONS OF LIQUID PRODUCTS FROM COAL HYDROGENATION

Modified forms of published type-analyses are applicable to high-boiling saturated and aromatic fractions from coal hydrogenation. Two type-analyses were applied to the urea raffinate of the saturated fractions. One, developed by R. J. CLERC, A. HOOD and M. J. O'NEAL[6], is relatively independent of structural variations within each saturated type. This method is based on the constancy of total ionization over a certain portion of the spectrum. The other, developed by H. E. LUMPKIN[7], does not determine mono-aromatics. Being based on the spectra of specific compounds found in petroleum, it is possibly not as independent of structural variations. However, it yields relative percentages of 2-, 3-, and 4-ring condensed *cyclo*paraffins.

To obtain molecular weight distributions, the low-ionizing-voltage technique, described by D. P. STEVENSON and C. D. WAGNER[8], H. E. LUMPKIN[9], and F. H. FIELD and S. H. HASTINGS[10] was applied to the saturated, aromatic, and tar acid fractions. Thus, the combined type-analysis and low-ionizing-voltage analysis provided total percentages for types of compounds and molecular weight distribution of these compounds. This approach gave detailed information for rapid product comparisons and required little preliminary processing of the samples. For the tar acid fractions, only the molecular weight distribution of the phenolic compounds was obtained. From the spectrum of the trimethylsilylether derivative, the presence of phenolic compounds of various structural types was verified.

Neutral material

The following results were obtained on a fraction of neutral middle oil,

Table 2. Urea complex (b.pt 260° to 276°C) of heptane eluate from neutral middle oil produced by hydrogenation of lignite

Parent molecular ions, m/e	*Relative peak intensity*	*Series C_nH_{2n-x}*		*Possible compound types*	*Type analysis Clerc's matrix (volume-per cent)*
		n	*x*		
196	—	14	0	*Naphthene*	4·2 *Non-condensed naphthene*
210	31·9	15	0		
224	10·2	16	0		
198	1·1	14	−2	*Paraffin*	94·0 *Paraffin*
212	287·5	15	−2		
226	136·5	16	−2		1·3 *Condensed naphthenes*
					0·3 *Mono-aromatic*
					0·2 *Naphthalenes*

Direct analysis from parent peaks
(Calculated as normal paraffins)

Paraffins	*Volume per cent*
n-C_{15}	30·9
n-C_{16}	60·3
Total	91·2

boiling range 260° to 276°C, produced by hydrogenating lignite. Chromatographic separations of the neutral material on silica gel produced concentrated fractions of saturated, aromatic, and polar materials. The saturates were further separated into mainly straight-chain and branch-chain fractions by urea treatment.

Saturated fraction—Table 2 shows analyses of the urea complex of the saturated fraction, obtained by type-analysis and by direct analysis of the paraffin parent peaks. A low-ionizing-voltage spectrum was not necessary as

Table 3. Urea raffinate (b.pt 260° to 276°C) of heptane eluate from neutral middle oil produced by hydrogenation of lignite

Parent molecular ions, m/e	*Relative intensity, peak height from low voltage run*	*Series C_nH_{2n-x}*		*Some possible compound types*	*Type analysis*	
		n	*x*		*Clerc's matrix (volume-per cent)*	*Lumpkin's matrix (mol-per cent)*
198	0·3	15	12	*Naphthalenes, paraffins**	8·3 *Paraffins*	5·8 *Paraffins*
212	0·4	16	12			
226	0·2	17 *or* 16	12 −2			
200	0·8	15	10	*Alkyl indenes*		
214	0·8	16	10			
228	0·4	17	10			
188	0·6	14	8	*Alkyl indans*	8·5 *Mono-aromatics*	
202	1·6	15	8			
216	2·0	16	8			
230	0·9	17	8			
244	0·2	18	8			
176	1·2	13	6	*Alkyl benzenes, condensed tetracyclo-naphthenes*		3·2 *4-Ring condensed naphthenes*
190	1·8	14	6			
204	4·3	15	6			
218	3·1	16	6			
232	1·3	17	6			
246	0·5	18	6		*Total*	
178	1·8	13	4	*Condensed tricyclo-naphthenes*	49·2† *Condensed naphthenes*	28·6 *3-Ring condensed naphthenes*
192	7·2	14	4			
206	12·2	15	4			
220	4·6	16	4			
234	1·2	17	4			
248	0·2	18	4			
180	1·4	13	2	*Condensed bicyclo-naphthenes (hydrindanes, decalins)*		32·8 *2-Ring condensed naphthenes*
194	2·0	14	2			
208	11·6	15	2			
222	4·1	16	2			
236	0·6	17	2			*Total: 64·6†*
250	0·1	18	2			*Condensed naphthenes*
182	1·0	13	0	*Single ring naphthenes*	34·0 *Non-condensed naphthenes*	29·6 *Non-condensed naphthenes*
196	0·8	14	0			
210	2·1	15	0			
224	1·9	16	0			
238	0·6	17	0			

* Peak intensities very low because of higher ionization potentials of paraffins.
† Total condensed naphthenes, aromatic-free basis.
Lumpkin matrix—64·6 per cent. Clerc matrix—53·8 per cent.

the spectrum obtained with 70 V electrons showed only C_{15} and C_{16} paraffin peaks. The total paraffin content of 94·0 per cent by type-analysis compares favourably with that of 91·2 per cent by direct analysis. The distribution shows approximately one third normal C_{15} and two thirds normal C_{16}. The low percentages obtained in the type analysis for condensed *cyclo*paraffins, mono-aromatics, and naphthalenes probably are erroneous.

Results on the corresponding urea raffinate are given in *Table 3*. It demonstrates the kind of result obtained by combining low-ionizing-voltage data (to determine the molecular weights) with normal-ionizing-voltage data (for type-analysis). Parent peaks can be grouped in series, differing by 14 mass units, and assigned to possible compound types as indicated by the type-analysis. In many instances, structures containing both 5- and 6-member rings are possible. In the tables only the more probable compounds have

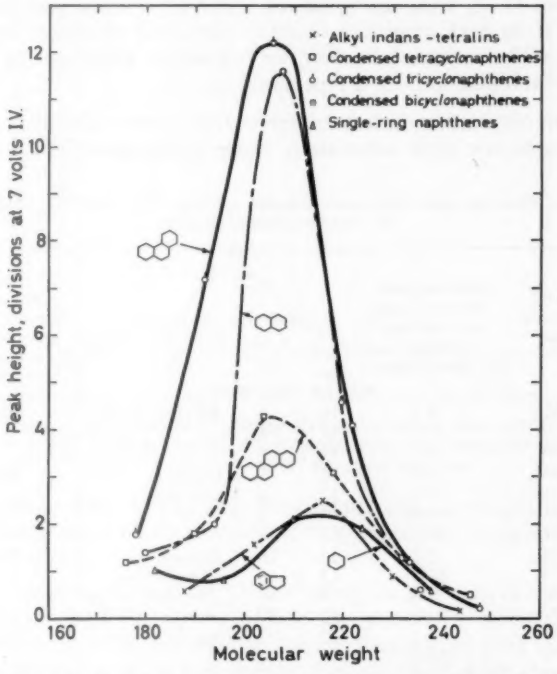

Figure 1. Identification of compound types in urea raffinate (260° to 276°C) of heptane eluate from neutral middle oil, produced by hydrogenation of a lignite. Low-ionizing-voltage mass spectrum

been shown. Though the relative peak intensities shown in *Figure 1* should not be associated directly with actual percentage of corresponding compounds, two facts are worth noting. First, the distribution of peak intensities from the low-ionizing-voltage run shows a regular progression in each series. Secondly, the maxima in most series occur at C_{15} or C_{16}, corresponding to the two

carbon numbers for the normal paraffins found in the urea complex. This urea raffinate sample shows seven homologous series comprised of 34 parent mass peaks. Molecular weights extend from 176 to 226. By the type-analysis matrix of Clerc, Hood and O'Neal[6] the sample was found to be approximately 50 per cent condensed naphthenes. By Lumpkin's matrix[7], condensed naphthenes were found to be about equally divided between 2- and 3-ring structures, with only a small percentage of 4-ring condensed naphthenes. Paraffins found by type analysis are presumably branched paraffins.

Aromatic fraction—Two type-analysis methods for analysing aromatics in petroleum have been described[11, 12]. Both methods determine the percentages of various 1- to 5-ring aromatic structures. Neither method is directly applicable to products from coal hydrogenation. The type-analysis matrix of F. W. MELPOLDER *et al.*[12] uses for calibration data average values for specific compounds found in the aromatic fraction of petroleum. S. H. HASTINGS, B. H. JOHNSON and H. E. LUMPKIN[11] derived sensitivity factors and interference coefficients from peak intensities found in particular aromatic fractions. As in the case of the saturated fraction, we followed a more general approach, based on total ionization, for a type analysis.

The results obtained in the last column in *Table 4* were calculated as follows. For a characteristic peak summation, those groupings chosen by Hastings

Table 4. Benzene eluate from neutral middle oil (b.pt 260° to 276°C) produced by hydrogenation of lignite

Parent molecular ions, m/e	*Relative peak intensity from low-ionizing-voltage spectrum*	C_nH_{2n-x}		*Some possible compound types*	*Type analysis from 70 V spectrum* (volume-per cent)*
		n	*x*		
162	0·5	12	6	*Alkyl benzenes*	10·3
176	1·1	13	6		
190	0·2	14	6		
160	2·8	12	8	*Indans, tetralins*	29·4
174	12·5	13	8		
188	10·4	14	8		
202	0·6	15	8		
158	2·1	12	10	*Indenes, dinaphthene-benzenes etc.*	17·2
172	32·0	13	10		
186	9·0	14	10		
200	0·5	15	10		
156	57·0	12	12	*Naphthalenes*	34·9
170	154·0	13	12		
184	7·9	14	12		
198	0·3	15	12		
154	23·3	12	14	*Acenaphthenes, diphenyls*	6·1
168	31·9	13	14		
182	4·0	14	14		
196	0·3	15	14		
152	1·4	12	16	*Acenaphthylenes*	2·1
166	1·4	13	16		
180	0·3	14	16		

* Reference 15

et al.[11] were used; that is, summation 91 for benzenes, 117 for indans and/or tetralins, 129 for dinaphthenes, etc., 141 for naphthalenes, and 167 for acenaphthenes. Sensitivities were based on the total ionization work of J. W. OTVOS and D. P. STEVENSON[13], and of R. J. CLERC, A. HOOD and M. J. O'NEAL[6]. G. F. CRABLE and N. D. COGGESHALL have shown that total ionization per unit liquid volume is essentially independent of molecular weight[14]. An extension of this work by G. L. KEARNS and G. F. CRABLE was applied to aromatics[15]. Molecular weight distributions for some possible structural types are shown in *Figure 2*. Parent peaks of 22 molecule-ions were found

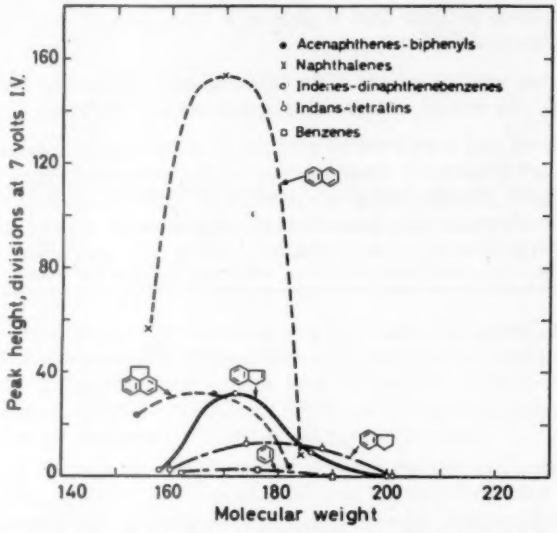

Figure 2. Identification of compound types in benzene eluate (260° to 276°C) from neutral middle oil, produced by hydrogenation of a lignite. Low-ionizing-voltage mass spectrum

ranging in mass from 152 to 202. Maximum peak intensities in the low-ionizing-voltage spectrum corresponded to compounds containing from 12 to 14 carbon atoms.

A detailed investigation of a synthetic blend has not been carried out, but the type-analysis used for aromatics has been shown by others to be independent of structural types. The polar fraction has not yet been investigated. Techniques similar to those used for the analysis of tar acids should be applicable.

Tar acids

Tar acid fractions obtained from the hydrogenation of lignite and also from low temperature tar have been investigated by the low-ionizing-voltage technique. Wide boiling fractions of tar acids can be characterized from the trimethylsilylether derivatives of the phenolic compounds. In many instances, trimethylsilylether spectra of the tar acid fractions are directly interpretable.

As reported by S. H. LANGER, S. CONNELL and I. WENDER[16], phenols form trimethylsilylether derivatives quantitatively

$$(CH_3)_3SiNHSi(CH_3)_3 + 2(R)OH \rightarrow 2(R)OSi(CH_3)_3 + NH_3$$

Indications are that the reaction is quantitative also for many other compounds found in the phenolic extract, including dihydric phenols. Formation of the trimethylsilylether derivative increases the mass of the parent molecule ion by 72 mass units (for each hydroxyl group) and produces a new series of peaks free from interference by other classes of compounds[17]. Thus complete removal of neutral material is not necessary. Spectra of the pure dihydric phenol derivatives indicate that as little as 0·1 per cent of these compounds should be detectable.

Low-ionizing-voltage spectra of the phenols were obtained at 7 V indicated (uncorrected), the actual voltage being approximately 10 V.

Results on tar acid samples show promise of being at least semiquantitative. However, even qualitative determination of the structural types present in various samples permits rapid comparison of samples of different origin. Sensitivity coefficients were obtained at reduced ionizing voltage for phenolic compounds representing several structural types. The coefficients shown in

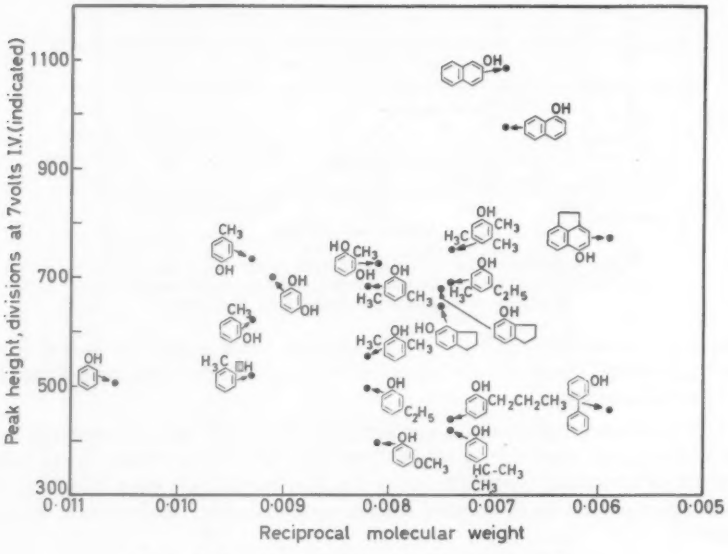

Figure 3. Sensitivities of phenols at low ionizing voltage

Figure 3 (plotted in manner described by Lumpkin) follow correlation schemes similar to those found by Lumpkin for aromatic compounds having alkyl substitution[9]. Sensitivity factors increased with the number of condensed aromatic rings and also with methyl substitution on the ring(s). Ethyl and propyl substitution resulted in progressive decreases in sensitivity. Other

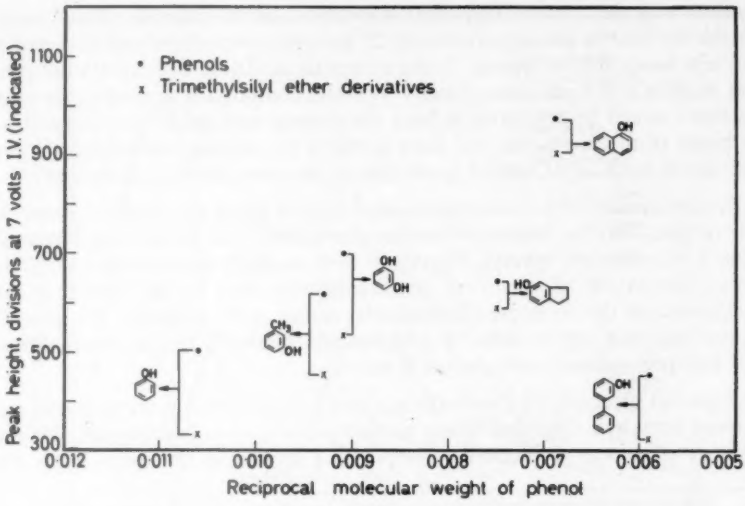

Figure 4. Sensitivities of phenols and their trimethylsilylether derivatives at low ionizing voltage

structural variations (e.g. a saturated ring or a methoxyl group) also resulted in reduced parent mass sensitivities. Excluding naphthol and structures having substituents larger than ethyl on a ring, sensitivity coefficients shown in *Figure 3* have a spread of 36 per cent. With an average sensitivity coefficient, semiquantitative analyses (±20 per cent) appear possible.

Sensitivity coefficients are shown in *Figure 4* for phenol, cresol, indanol, phenylphenol, naphthol, resorcinol, and their trimethylsilylether derivatives. There appears to be a definite correlation between the sensitivities of the

Table 5. Low-ionizing-voltage analysis of a synthetic mixture of phenols (volume per cent)

Compound	*Mass spectrometer analyses*		*Synthetic*
	As phenols	*As trimethyl-silylether derivatives*	
m-*Cresol*	30·3	28·6	31·3
m-*Ethylphenol*	22·2	22·1*	21·1
3-Ethyl-5-methylphenol	5·9	6·1*	5·9
Resorcinol	10·1	12·7	12·1
2-Methylresorcinol	4·7	5·1*	5·1
5-Indanol	8·3	7·6	8·2
α-*Naphthol*	5·7	5·5	5·5
5-Acenaphthenol } m-*Phenylphenol* }	11·6†	11·2†	9·9
1-Pyrenol	1·2	1·1*	0·9

* Sensitivity of trimethylsilylether based on correlation with phenol sensitivity (see *Figure 4*).
† Both compounds have molecular weight of 170; weighted sensitivity used.

phenols and the trimethylsilylether derivatives of the phenols. Coefficients for the derivatives are approximately 25 per cent lower for single ring and 8 per cent lower for condensed 2-ring compounds. These coefficients indicate that as little as 0·1 per cent of many phenolic compounds present in tar acid fractions should be detectable in both the original and the derivative spectra. In many instances, it has not been possible to prepare trimethylsilylether derivatives because of limited quantities of the pure phenolic compounds.

Results obtained on a 10-component synthetic blend are shown in *Table 5*. The original and the trimethylsilylether derivative of the blend were analysed from 7 V (indicated) spectra. Results of both analyses were satisfactory. The above correlation of sensitivity coefficients was used to obtain the values designated in the footnote. Reasonable values were obtained for several major types of compounds in tar acid fractions, showing that a semiquantitative interpretation of such spectra is valid.

A partial spectrum of a trimethylsilylether derivative of a tar acid fraction derived from hydrogenated lignite is shown in *Figure 5*. Parent peaks for the derivatives appear at masses corresponding to the homologous series for

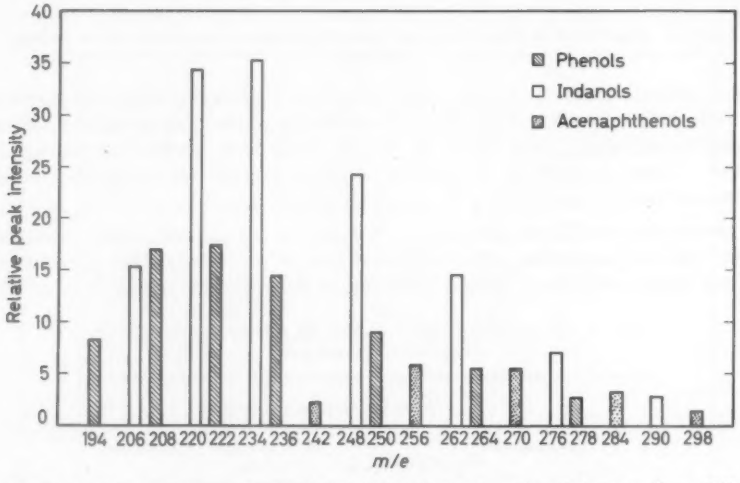

Figure 5. Mass spectrum of trimethylsilylether derivative—phenol fraction (b.pt 273° to 340°C) of middle oil from hydrogenation of lignite (ionizing voltage 7 V indicated)

phenols, indanols, and acenaphthenols. A tar acid fraction containing material boiling up to approximately 300°C was investigated in detail. A small amount of neutral material was present as indicated by peaks corresponding to the molecular weights of acenaphthenes and/or diphenyls. Molecule-ion peaks in the original spectrum were verified as being phenolic from the spectrum of the trimethylsilylether derivative sample. The original spectrum showed eight series of parent-mass-peaks ranging from mass 94 to 234. Appearance of the peaks of the trimethylsilylether derivatives at the correct parent masses verified the presence of several structural types. *Figure 6* shows the new series

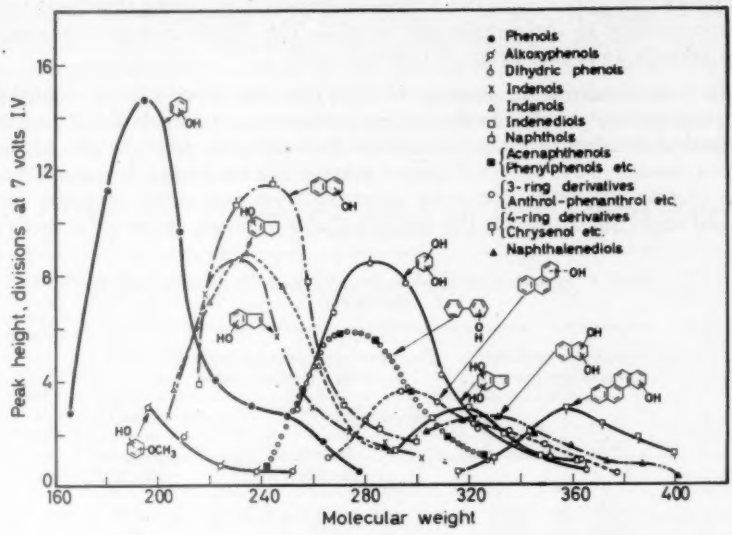

Figure 6. Identification of compound types in methanol-extracted fraction of low-temperature tar from a lignite. Trimethylsilylether derivative mass spectrum

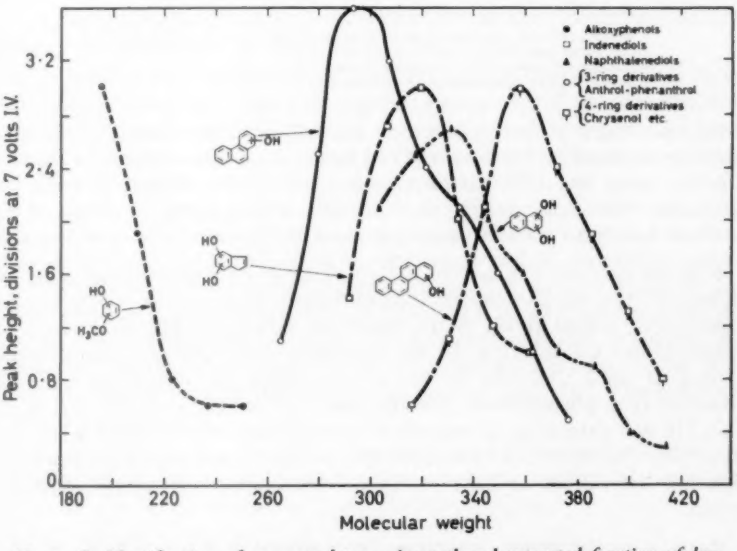

Figure 7. Identification of compound types in methanol-extracted fraction of low-temperature tar from a lignite. Trimethylsilylether derivative mass spectrum

of peaks that appeared in the derivative spectrum and some structural types corresponding to these molecular weights. The higher boiling components are presented in more detail in *Figure 7*.

In some instances, the presence of more than one structural type contributing to a particular series in the original spectrum, could be detected from the trimethylsilylether derivative spectrum. For example, dihydric phenols and alkoxyphenols have identical parent mass peaks beginning at mass 124. In the trimethylsilylether derivative spectrum, two new series of peaks were found beginning at masses 196 and 254 (*Table 6*). Thus, the original series of

Table 6. Identification of phenolic compounds by trimethylsilylether derivatives

Series in original mass spectrum		*Two new series in mass spectrum of trimethylsilylether derivatives*			
		*Alkoxyphenols**		*Dihydric phenols†*	
m/e	*Relative intensity*	*m/e*	*Relative intensity*	*m/e*	*Relative intensity*
110	5·0			254	2·9
124	4·3	196	3·0	268	6·6
138	4·1	210	1·9	282	8·5
152	3·1	224	0·8	296	7·7
166	1·6	238	0·6	310	4·2
180	1·0	252	0·6	324	2·2
194	0·8			338	1·6
208	0·5			352	1·1
				366	0·6

* Trimethylsilylether derivative series corresponds to addition of one $Si(CH_3)_3$ group indicating alkoxyphenols (e.g. guaiacols).
† Trimethylsilylether derivative series corresponds to addition of two $Si(CH_3)_3$ groups indicating dihydric phenols (e.g. resorcinol).

peaks including masses 124, 138, etc., were resolved into two series of structural types containing both one and two hydroxyl groups. A similar separation into two series was effected for a parent mass series starting at mass 134. Derivative mass-ions starting at mass 206 corresponded to indanols and tetralols. A derivative series starting at mass 292 corresponded to indenediols.

With the exception of parent mass series having contributions from two structural types, peak intensities formed smooth progressions. For the phenol homologues, parent peaks in the spectrum indicated addition of up to 10 carbon atoms on the ring. In the derivative spectrum, a series of peaks starting at mass 266 was found, corresponding to derivatives of 3-ring structures (e.g. phenanthrol). Another series of derivative peaks, starting at mass 316 and extending to mass 414, corresponded to the 4-ring series (e.g. chrysenol). Eleven of the 12 series in the spectrum were shown by trimethylsilylether derivatives to have structures containing one or two hydroxyl groups.

Maxima for the various structural types shown in *Figure 6* occur with the equivalent of two methylene groups substituted on the ring(s). As described

previously, phenols having up to ethyl substitution show variations in sensitivity coefficients of ±20 per cent. Thus, the maximum peak intensity indicates the carbon number of maximum percentage for phenols and probably other structural types. The distribution data for phenols shown in *Table 7* were obtained using average sensitivity factors based on the data given in *Figure 3.* Further study of sensitivity factors should result in quantitative data for the other structural types shown in *Figures 6* and *7.*

Table 7. Quantitative carbon number distribution of alkyl phenols in methanol-extracted fraction of low-temperature tar from a lignite

Carbon number	6	7	8	9	10
Molecular weight	94	108	122	136	150
Volume per cent of tar acid fraction	3·8	7·1	6·9	3·7	1·4
Carbon number	11	12	13	14	
Molecular weight	164	178	192	206	
Volume per cent of tar acid fraction	1·1	0·9	0·5	0·3	(25·7)

SUMMARY

Mass spectrometric methods have been developed for the analysis of saturated, aromatic, and tar acid fractions of oils derived from coal. The methods described require samples separated only as to compound types. The saturated and aromatic fractions of neutral material are characterized by determining the total percentage of each structural type and the molecular weight distribution of these compounds. This is done by combining data from a conventional mass spectrometric type-analysis with data obtained from a low-ionizing-voltage mass spectrum. The polar material resulting from an elution chromatography separation has not been investigated as yet.

Mass spectrometric methods for determining the structural types in tar acid fractions have also been investigated. Formation of the trimethylsilyl-ether derivatives permits identification of various phenolic types, even in the presence of neutral material. Certain structural types forming identical homologous series, but differing in the number of hydroxyl groups on the ring structure, can be identified in the trimethylsilylether derivative spectrum. An example of this is the dihydric- and alkoxy-phenols. Application of this technique has been made to tar acid fractions produced by coal carbonization, to investigations of coal hydrogenation neutral and tar acid material, and to de-alkylation studies. Quantitative carbon number distribution data have been obtained for alkylphenols having up to 14 carbon atoms. It appears that carbon number distribution data can also be obtained for many of the other structural types in tar acid fractions of oils derived from coal. This investigation is being continued.

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Central Experiment Station,
Bureau of Mines, Region V,
Bruceton, Pa, U.S.A.

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Effect of Ferrocene on Carbon Formation from Acetylene

J. D. FRAZEE and R. C. ANDERSON

The effect of adding Ferrocene was studied in contrast to that of other additives tested in decomposition and carbon formation reactions with acetylene. This effect was found to involve surface reactions. Experimental details and qualitative results are described. Fine particles of iron can decrease general carbon formation.

IN recent years Ferrocene (di*cyclo*pentadienyliron) and related compounds have been under extensive investigation, both as interesting examples of metallic complexes and as substances of practical usefulness as fuel additives. It has been noted that the Ferrocene is quite effective as an inhibitor of carbon formation[1]. It was of interest, therefore, to study the effect of this compound as contrasted to others which have been tested in this laboratory as additives in decomposition and carbon formation from acetylene[2]. This became of particular interest when it was found that addition of Ferrocene to acetylene tended to accelerate flame propagation in acetylene, where the flame propagation occurs because of decomposition of the acetylene, with carbon or soot as a major product[3].

The pyrolysis of acetylene–Ferrocene mixtures in a flow reactor was studied. The effect of Ferrocene was found to involve surface reactions; so it is extremely difficult to get quantitative and reproducible data; but the qualitative results described below do give an interesting insight into the mechanism of its action.

EXPERIMENTAL DETAILS

The Ferrocene was a research sample furnished by courtesy of E. I. du Pont de Nemours and Company. The acetylene used in these experiments was obtained from commercial sources. Acetone was removed by treatment with sodium hyposulphite ($Na_2S_2O_6$). The gas was then dried over anhydrous calcium sulphate. The iron metal was in the form of a fine powder and had been reduced with hydrogen. The helium was Grade A, from the U.S. Bureau of Mines.

The reactor was designed in such a way as to permit essential separation of the various effects. It consisted of a long (1·5 cm × 75 cm) Vycor tube externally heated with Chromel resistance wire coils and wrapped with plaster–asbestos insulation. The reactor had three separate heating zones. The first of these heating zones was used to vaporize the Ferrocene. The other two zones were used for the 700°C reaction zones. The desired surface temperatures were obtained by using variable transformers.

Individually calibrated manometers (helium, acetylene, air) were used to control the flow of gas. The concentration of Ferrocene vapour was determined by prior calibration on a weight-loss basis. The flowrate of Ferrocene was expressed in volume per unit time (cm^3/min) taken from the mole weight.

The Ferrocene was introduced from a 2 g sample in a porcelain boat placed in the calibrated heating zone adjacent to and upstream from the reaction zones. The helium carrier

gas entered at one end and passed the length of the tube. The acetylene could be admitted with the helium or further downstream as desired. When iron powder, iron oxide powder, or white sea sand was used, 2 to 3 g were spread over the length of the reaction zone in the flow reactor.

Samples of suspended matter in the product gases could be taken by passing the gas through Millipore filters of AA porosity. Analyses of the gaseous products were made with a recording gas-chromatography unit. A 30 ft column of activated charcoal with nitrogen carrier gas was used for the hydrogen analysis. A 10 ft column of Curtin's Universal X3 with helium carrier gas was used for the benzene analysis. Since the relative amounts of gaseous products were the point of primary interest, the results were expressed in units of scale deflection.

The temperature and flowrates could be satisfactorily controlled. The principal source of error lay in the varying condition of the reactor surface. Between runs the reactor was vigorously cleaned with a boiling solution of Alconox, followed by scrubbing with acetone, and rinsing with distilled water. If this did not suffice, the reactor was heated and blasted with air overnight and then rewashed.

To get a comparison of the effect of the *gaseous* products formed from the Ferrocene with that of the solids, the three-zone reactor was used. A glass wool plug was inserted in the cool region between the two reaction zones. The Ferrocene was vaporized and passed through the first hot zone. The heavy materials then collected on the glass wool plug in the cool region and the gases went on to the second hot zone and there mixed with acetylene. The cool zone effectively condensed most of the iron compounds and unreacted Ferrocene.

In another case the Ferrocene was entirely vaporized and passed through the first hot zone and then the acetylene was admitted with the helium and passed through this same zone, over the hot deposit of Ferrocene deomposition products and into the second zone which was cool. The acetylene contact time was the same, essentially, in both cases (cf. items 2 and 7, *Table 1*).

When approximately 2 per cent Ferrocene is added to 60 per cent acetylene at 700°C the initial effect is to change the appearance of the exhaust from a white fog (of polymer deposits) with acetylene alone to a dark brown or black exhaust (containing soot). After several minutes the smoke disappears. Upon examining the inside of the reactor a hard deposit of iron, carbon black, and vitreous carbon is observed. If the reaction is allowed to continue the reactor becomes clogged.

Table 1. Surface effects

Reactants			*Gas products*		*Observations on exhaust*
Helium (cm^3/*min*)	C_2H_2 (cm^3/*min*)	*Other materials*	H_2 (*scale reading*)	*Benzene (scale reading)*	
120	180	*None*	3	60	*Thick white fog, extensive polymer condensation downstream*
120	180	*Iron deposit from Ferrocene*	>100	13	*No fog, very little polymer*
120	180	*Powdered Fe*	>100	32	*No fog, very little polymer*
120	180	*Sea sand*	5	45	*Medium thick white fog, some polymer condensation*
120	180	*6 cm^3/min Ferrocene*	>100	47	*Thick, very dark smoke, some polymer condensation, positive iron test for exhaust gas*
300	*None*	*6 cm^3/min Ferrocene*	0	0	*Thin white fog, very little polymer*
120	180	*Gaseous reaction products from 6 cm^3/min Ferrocene*	3	55	*Thick white fog, extensive polymer condensation*

Further results for a variety of conditions are shown in *Table 1*. All of these tests were made with the flow reactor at 700°C. In other tests air was substituted for part of the helium and found to have no observable influence on the effect of the Ferrocene as an additive. Powdered iron oxide gave results similar to those with the iron. The appearance of the deposits collected on filters were in accord with the visual observations—showing a decrease in carbon particles when the smoke was thinned out.

The initial effect of the Ferrocene is to accelerate decomposition and carbon formation. This is in accord with the results in flame tests and may be attributed to decomposition of the Ferrocene to give *cyclo*pentadienyl radicals or other active fragments which can enhance the acetylene reaction.

The *gaseous* reaction products from Ferrocene have no particular effect on the acetylene; but as soon as a deposit appears—either in the course of reaction or by deposition beforehand—there is quenching of the formation of smoke and carbon. The tests with sea sand and iron powder confirm that this is a surface effect specific to the iron particles or deposits. An interesting feature of the results is the effect of the deposits in increasing the hydrogen production but decreasing that of benzene.

These observations show that fine particles of the iron, or surface deposits, are effective in decreasing general carbon formation. They do not, of course, eliminate the possibility that iron compounds in the gas phase have some effect. The initial acceleration, however, suggests that some condensation and aggregation is necessary for effective inhibition.

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Department of Chemistry,
University of Texas,
Austin 12, Texas, U.S.A.

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Diffusion of Carbon Dioxide from Coal

B. A. BOLT* and J. A. INNES†

Rates of desorption of carbon dioxide at 38°C from coals of varying type and rank have been measured. Micropore diffusion coefficients, estimated from the desorption/time curves, are of the order of 10^{-7} cm²/s. The results are compared with those of other workers.

THE aims of the present study were (*i*) to measure the rates of desorption of carbon dioxide from the fine pore structure of a range of coal samples at normal temperatures; and (*ii*) to correlate the results with the coal type and rank. Previous workers[1, 2] have assembled evidence that, under certain physical conditions, the diffusion of gases through the fine pore structure of coal resembles that through zeolites[3]. Estimation of the micropore diffusion coefficient D for a particular coal sample is, however, complicated by the presence of cleat and other macroscopic cracks in the coal material. The effect of these 'macropores' was reduced in this experiment by crushing the coal samples to a particle size range of mean radius 0·0126 cm. (P. ZWIETERING and D. W. VAN KREVELEN[2] have suggested that the radius of a micropore is about 10 Å.)

The particular coal samples and carbon dioxide gas were chosen because of associated investigations into gas outbursts in mines.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used is illustrated in *Figure 1*.

The sorption vessel 4 (maintained at a steady temperature of 38°C) contained crushed coal of known weight (≈ 15 g), which had been dried in an air oven at 105°C and degassed to about 10^{-2} mm of mercury. Carbon dioxide was admitted until equilibrium was established at the desired pressure. The sorption vessel was then sealed. After a short time the vessel was suddenly opened, allowing the rapid release of gas into the chamber 3 which contained water. The gas volume was successively measured at atmospheric temperature and pressure by continuous vertical adjustments of the column 2. Volumes were read to the nearest 0·5 cm³. Corrections were applied for the quantity of gas occupying the free volume of the system and the compressibility of carbon dioxide gas. All measured volumes were recorded as their n.t.p. equivalent. It was found that a thin kerosene film on the water prevented the absorption of gas during the course of desorption; the desorption usually occupied 40 to 50 minutes before effective completion.

RESULTS

The experiment was repeated for each of the twelve coal samples shown in

* Department of Applied Mathematics, University of Sydney.
† Department of Mining Engineering, University of Sydney. Present address: c/o Central Research Laboratories, B.H.P., Shortland, N.S.W.

Table 1, commencing from initial pressures of 11 and 6 atmospheres in each case. Typical desorption/time curves for an initial pressure of 11 atmospheres are shown in *Figure 2*. After 10 to 15 seconds the curves become concave towards the time axis and the desorbed volume, v, steadily approaches the final equilibrium value v_∞, for the adopted temperature and pressure.

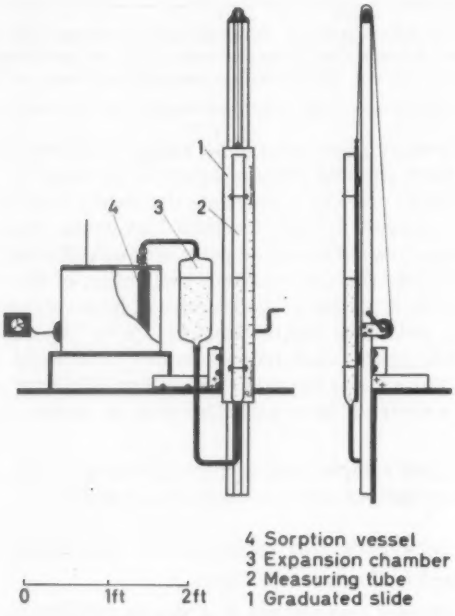

Figure 1. Diagrammatic representation of desorption apparatus

For $t < 30$ sec, measurements have relatively low precision, owing to the initially high rate of desorption at 38°C. Consequently the curves were fitted at $t = 1$ min, $t = 5$ min and $t = \infty$, to the algebraic form

$$v = v_\infty[1 - A \exp(-\lambda t)] \quad \ldots . [1]$$

where v_∞, A and λ were the parameters determined. In each case the differences between the calculated and observed values of v, using the calculated A and λ in equation 1, did not exceed 5 per cent so long as t exceeded 30 sec. The computed values of A and λ for the twelve samples are given in *Table 1*.

All coal samples were crushed to a particle size of $-48 + 65$ Tyler mesh (mean radius 0·0126 cm), except for Duroclarain (2) which was crushed to $-35 + 42$ Tyler mesh (0·0192 cm). Values of A and λ from two desorptions of Collinsville State Sample (1) and Elk River, at 11 atm, are listed to indicate the experimental uncertainties; with further refinements in apparatus these can probably be reduced consistently to less than 10 per cent.

Table 1

Coal	*Pressure atm*	*A*	*λ*	$D \times 10^{-7}$
(a) *Staatsmijnen Emma (Holland)*	11·0 6·0	0·580 0·650	0·130 0·124	0·35
(b) *Duroclarain (2) from Metropolitan, N.S.W. (−35 + 42) Tyler*	11·0 6·0	0·603 0·630	0·150 0·163	0·92
(c) *Collinsville State (Qld) Sample (1)*	11·0 11·0 6·0	0·459 0·468 0·526	0·166 0·161 0·157	0·43
Sample (2)	11·0	0·512	0·159	
(d) *Bowen Consolidated (Qld)*	11·0 6·0	0·554 0·600	0·168 0·176	0·45
(e) *Excelsior (N.S.W.)*	11·0 6·0	0·595 0·645	0·181 0·174	0·48
(f) *Duroclarain (1) from Metropolitan (N.S.W.) (−48 + 65) Tyler*	11·0 6·0	0·537 0·572	0·182 0·193	0·48
(g) *Anthracite from Great Mountain (Wales)*	11·0 6·0	0·548 0·566	0·202 0·186	0·54
(h) *Vitrain from Wonthaggi (Victoria)*	11·0 6·0	0·566 0·605	0·216 0·183	0·58
(i) *Canmore (Canada)*	11·0 6·0	0·435 0·464	0·212 0·213	0·57
(j) *Durain from Liddell Seam (N.S.W.)*	11·0 6·0	0·272 0·261	0·265 0·261	0·71
(k) *Elk River (Canada)*	11·0 11·0 6·0	0·238 0·212 0·210	0·280 0·315 0·290	0·80

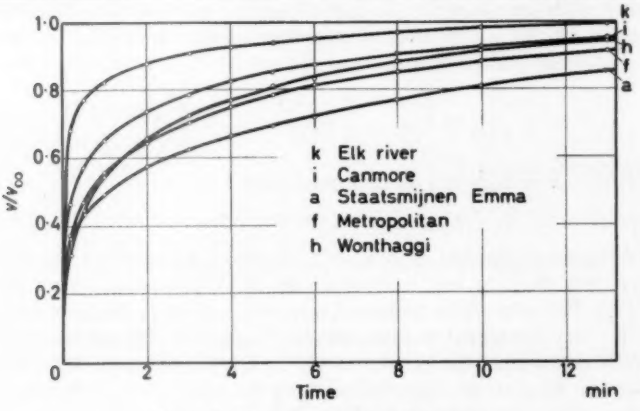

Figure 2. Examples of desorption curves

DISCUSSION

From the classical theory of diffusion[4], desorption from an isotropic sphere, radius a, which has initially a uniform concentration of gas throughout, is

$$v = v_\infty[1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-Dn^2\pi^2 t/a^2)] \quad \ldots . [2]$$

provided the surface concentration remains constant. R. M. BARRER[3] has shown that equation 2 holds also for a powder of spherical particles of the same size. To a first approximation, equation 2 may be written

$$v = v_\infty[1 - 0{\cdot}6 \exp(-\pi^2 Dt/a^2)] \quad \ldots . [3]$$

The second term in the summation in equation 2 is only 0·1 of the first term when $t = 1$ min, $D = 10^{-7}$, so that identification of equations 1 and 3 allows approximate values of D to be estimated. We note, incidentally, that the values of A in *Table 1* approach 0·6 except for coals (j) and (k). These coals have a high initial rate of degasification, probably mainly due to a more developed macropore structure. Wherever the estimated value of A is much less than 0·6, it seems likely that determination of a diffusion coefficient, D, using the approximation 3 will be unsatisfactory. Nevertheless, the calculated values of D have some interest in comparison with other estimates, and hence are included in *Table 1*.

The calculated values of D are of the order of 10^{-7} to 10^{-8} cm²/s; for $-48 + 65$ Tyler mesh and 11 atm, D lies between $0{\cdot}35 \times 10^{-7}$ cm²/s (Emma) and $0{\cdot}80 \times 10^{-7}$ cm²/s (Elk River). Variations of D with pressure are probably within the experimental errors. The diffusion coefficients for the finer and coarser duroclarains ($D = 0{\cdot}48 \times 10^{-7}$ and $D = 0{\cdot}92 \times 10^{-7}$ cm²/s, respectively) reflect the expected increased effect of macropores in larger particles.

It is worth remarking that the method used by J. CRANK and G. S. PARK[5] to determine D from an experimental diffusion/time curve gives reasonable agreement with the value for the Emma sample given above. From the first three terms of the summation in equation 2, the value of t/a^2 for which $v/v_\infty = 0{\cdot}5$, is given by

$$\frac{1}{\pi^2 D} \ln\left[\frac{\pi^2}{12} - \frac{1}{4}\left(\frac{\pi^2}{12}\right)^4 - \frac{1}{9}\left(\frac{\pi^2}{12}\right)^9\right] \quad \ldots . [4]$$

to about the same accuracy as approximation 3.

Hence $D \approx 0{\cdot}035\, a^2/t_{0{\cdot}5}$, where $t_{0{\cdot}5}$ is the time at which $v/v_\infty = 0{\cdot}5$.

The diffusion coefficient at 20°C of methane in a sample of vitrinite (rank 88·6 per cent carbon) has been given by P. ZWIETERING *et al.*[6] as about 10^{-12} cm²/s. From carefully measured sorption rates at low temperatures (134° to 157°K) they calculated D using the BET value for the macropore surface area and extrapolated the results to 20°C. The discrepancy with the above results is too large to be explained only on the basis of the difference in size between carbon dioxide and methane molecules. The surface area adopted

by Zwietering would need to be changed by a factor of 10^{-2} to obtain agreement with the magnitude of D estimated above.

However, the systems are so different that a direct comparison is not entirely relevant.

A description of the coal samples used here is given in *Table 2*. A comparison with *Table 1* shows that there is no clear correlation between values of λ and either type or rank. The very dull coals, Emma and Liddell durain, for example, have nearly the extreme values of D. It is notable that Collinsville State and Bowen Consolidated, both from the Bowen Seam in Queensland, have almost identical diffusion coefficients; similarly with Excelsior and Metropolitan (−48 + 65 Tyler), both from the Bulli Seam, N.S.W.

Table 2

Coal	*Type*	*Proximate analysis (dry basis)*		
		Fixed C %	*Volatiles* %	*Ash* %
(a) *Staatsmijnen Emma*	*Durain*	62·9	18·4	18·7
(b) *Metropolitan (N.S.W.)*	*Duroclarain*	69·3	19·4	11·3
(c) *Collinsville State (Qld)*	*Duroclarain*	59·2	21·8	19·0
(d) *Bowen Consolidated (Qld)*	*Duroclarain*	65·7	20·6	13·7
(e) *Excelsior (N.S.W.)*	*Duroclarian*	67·3	23·2	9·5
(g) *Great Mountain (Wales)*		92·5	5·7	1·8
(h) *Wonthaggi (Victoria)*	*Vitrain*	64·9	33·6	1·5
(i) *Canmore (Canada)*	*Clarain*	85·1	12·0	2·9
(j) *Liddell Seam (N.S.W.)*	*Durain*	50·6	29·4	20·0
(k) *Elk River (Canada)*	*Duroclarain*	68·4	18·2	13·4

Both Emma and Elk River coals, like several others in the list, are subject to instantaneous outbursting. The marked difference in the diffusivities of these two coals suggests that diffusivity is not a dominant factor in the mechanism of outbursts. The results, although tentative, also suggest that micropore diffusion characteristics of coal are not mainly sensitive to chemical composition but depend considerably upon the fine structure of the coal which has been determined by the physical history of the seam.

The University of Sydney,
Sydney, Australia

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Studies in Bomb Calorimetry XI—Determination of the Calorific Value of Gases; Miscellaneous

R. A. MOTT and C. PARKER

An account is given of the use of a bomb calorimeter for determining the calorific value of Calor gas and town gas. The volume of gas used can be estimated with greater precision than when using a flow-type calorimeter. The temperature rise with Calor gas can be measured satisfactorily with a mercury-in-glass bomb-calorimeter thermometer, but with town gas a resistance thermometer is desirable. It is suggested that the method should be used for determinations of the calorific value of unpurified coal gas, and as a basis for the calibration of flow-type calorimeters, which are liable to be biased. In general bomb calorimetry, recommendations are made on the heat of ignition, the nitric acid correction, the high-pressure bomb, temperature measurement, crucibles, the pressure gauge, the benzoic acid and the weighing errors. Descriptions are given of a bomb whose cap may be tightened by hand and of a timer–tapper system.

THE present paper, which concludes the series, at least for the present time, deals first with the use of a bomb calorimeter for the determination of the calorific value of gases and then with miscellaneous subjects.

Many of the conclusions from this series have been accepted as a basis for recommendations of procedure in *B.S. 1016:* Part 5[1], the *Draft Recommendation*[2] of the International Organization for Standardization (ISO), and *I.P. 12/58 T*[3]. The format of *B.S. 1016:* Part 5 may be conveniently used for reporting the miscellaneous experimental data and making further recommendations based on our extensive experience.

DETERMINATION OF THE CALORIFIC VALUE OF GASES

The calorific value of town gas is usually determined by a recording calorimeter. This must be checked periodically by a gas examiner using a Boys flow-type calorimeter which, unlike the bomb calorimeter, is not standardized by the use of a material of certified calorific value. In the flow-type calorimeter the percentage error of temperature measurement is minimized by the use of a higher temperature rise than in a bomb calorimeter (20 °C instead of 3 °C) and the chief source of error lies in the measurement of the quantity of fuel, for which a wet meter is used. In the *Gas Examiners' General Directions 1956*[4], it is stipulated that the gas examiner must at least once a year check the meter against a Hyde standard reference meter and meter comparator, a difference of 0·3 per cent being tolerated. Other sources of error, such as incomplete combustion and the thermal effect of corrosion, may introduce a bias, so that good replication is not proof of high accuracy.

When testing a solid or liquid fuel in a bomb calorimeter, which can be made bias-free (as is the Griffin–B.C.R.A. Isothermal Calorimeter), the weights

of samples may be measured to within ± 0·02 per cent by using a good analytical balance and an accurate set of weights. The standard deviation with a pure substance, using a mercury-in-glass bomb-calorimeter thermometer, may be as low as 0·15 per cent. Temperature measurement is the greatest source of error and the standard deviation may be reduced to 0·08 per cent, or less, by the use of a resistance thermometer.

It seemed possible that a bomb calorimeter could be used for the accurate determination of the calorific value of a rich gas (e.g. butane), with which a temperature rise of about 3°C would be obtained, and that even for town gas its use might be satisfactory if a resistance thermometer were used for measuring the temperature rise. M. D. ZHUKOVSKAYA[5] has reported work in this field. A preliminary report of similar work by the British Coke Research Association is given here.

Measurement of the capacity of a bomb

The capacity (approximately 320 ml) of a Griffin–B.C.R.A. bomb, which is fitted with a Schrader valve, was determined as follows. The bomb was cleaned inside and outside with carbon tetrachloride, dried and weighed on a heavy-duty balance, the ambient temperature, relative humidity and atmospheric pressure being noted at the same time. The bomb cup was then filled with distilled water which had been boiled and cooled, an additional precaution being that the cooled water, contained in a Winchester, was subjected to suction from an Edwards vacuum pump. All adhering air bubbles in the cap were removed with a pointer; the bomb cap was then carefully fitted and the union nut screwed down, the Schrader valve being opened to allow excess water to escape until further hand-tightening was impossible. The bomb was dried externally and weighed, the temperature being noted. From the difference in weight, the weight of a volume of air at the temperature, pressure and relative humidity of the first weighing was deducted. The weight of water so obtained was converted to volume, using the density at the temperature of the second weighing. Several repeat determinations were made and the mean capacity calculated. Two series of determinations were made, the first with the normal bomb and the second after a collar had been fitted, as will be described later. The results are recorded in *Table 1*.

Table 1. Capacity (ml) of Griffin–B.C.R.A. bomb

Test No.	*Series I*	*Series II (with collar)*
1	320·13	319·22
2	320·19	319·46
3	320·19	319·10
4	320·19	319·30
5	320·19	
6	320·33	
7	320·35	
8	319·95	
Mean	320·19	319·22
σ	0·123 = 0·038%	0·151 = 0·047%

Thus the capacity can be measured with a standard deviation (σ) of under 0·05 per cent. This is the determining factor in the accuracy of measurement of the quantity of gas burnt, and is much better than when using a flow-type calorimeter with a wet meter.

Determination of the calorific value of Calor gas using a mercury-in-glass thermometer

Our first determinations of calorific value using the bomb calorimeter were made on Calor gas (butane). To ensure that the air was completely displaced from the bomb, it was subjected to repeated filling and exhaustion in the apparatus illustrated diagrammatically in *Figure 1*(a). The union connection to the bomb is shown in *Figure 1*(b); it incorporated a plunger for opening

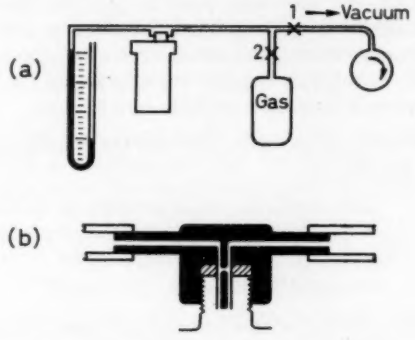

Figure 1.
(a) *Apparatus for filling calorimeter bomb with gas*
(b) *Connection to bomb, showing plunger for opening and closing Schrader valve*

and closing the Schrader valve. With valve 2 closed the bomb was evacuated and, with valve 1 closed and valve 2 opened, the bomb was filled with gas to a gauge pressure of 20 cm of mercury, valve 2 then being closed. This was repeated four times and the Schrader valve then closed by giving the union one quarter turn.

The bomb was stood in the calorimeter and allowed to reach thermal equilibrium (10 min), the excess of pressure above atmospheric being released by depressing the Schrader valve. The temperature of the calorimeter and the atmospheric pressure were noted for the correction of the volume of gas to the standard conditions. Oxygen was then admitted to the bomb to the required pressure and a further standing period of 10 min allowed (to ensure good mixing of the fuel gas and the oxygen) before starting the determination of calorific value, which was carried out as in a conventional test on a solid or liquid fuel.

The crack which was heard on firing the charge indicated that the combustion was explosive. This explosive combustion tended to displace the calorimeter lid, and it was found that a flame issued momentarily from the Schrader valve. To overcome these effects, a cap was screwed over the Schrader valve; a plug of insulating material, 0·5 cm² in area, was placed below the centre of the base of the calorimeter vessel to damp down its vibration; and the ignition spring between the lid of the calorimeter vessel and the bomb was

replaced by a stiffer one. In subsequent tests, no displacement of the lid occurred.

In the combustion the 36 s.w.g. nickel–chromium firing wire was completely melted, instead of breaking as with solid and liquid fuels, and thinner wires were therefore tried. By trial and error it was found that 40 s.w.g. nickel–chromium wire could be used without a length of cotton, and that this thinner wire gave less disfigurement of the bomb on melting.

At first, an initial oxygen pressure of 7 atm (gauge) was used, but this was subsequently increased to 10 and then to 12 atm. At 10 atm soot was occasionally found in the bomb, but at 12 atm the combustion was never visually incomplete.

Since the standard quantity for the reporting of the calorific value of gaseous fuels in the United Kingdom is unit volume measured at 60°F and 30 in of mercury, and saturated with water vapour, a metal vessel containing water to saturate the gas was introduced into the filling system [*Figure 1* (a)] between the cylinder and the bomb.

A series of six determinations under satisfactory conditions gave the following results.

> Gross calorific value at constant volume and 12 atm (gauge) pressure = 3074 mean B.t.u./ft³ measured at 60°F and 30 in of mercury, and saturated with water vapour.
> Standard deviation = 20 B.t.u./ft³ = 0·66 per cent.

Comparison of this or any other mean value with a mean from tests on the same gas in the Boys calorimeter would necessitate two corrections, as described below.

(*1*) Adjustment to the constant-pressure conditions of the Boys calorimeter: this requires knowledge of the composition of the gas. For an average town gas, the quantity to be added to the constant-volume value is about 4·5 B.t.u./ft³.

(*2*) Adjustment to the pressure [0 atm(gauge)] of test in the Boys calorimeter: strictly, this also requires knowledge of the composition of the gas, but for all practical purposes a constant value can be assumed to apply to a given bomb; for a pressure of determination of 12 atm (gauge), 2·0 cal should be subtracted from the measured heat release in the combustion, i.e. $0{\cdot}00794/V$ B.t.u./ft³ should be subtracted from the calorific value, where V is the capacity of the bomb in ft³. For the bomb used in the present work, this is equal to 0·7 B.t.u./ft³. The net correction for town gas is therefore an addition of 4·5 − 0·7 = 3·8 B.t.u./ft³.

In fact, these corrections have not been applied to the values reported here, as repeatability has so far been our chief concern.

A further difference between the conditions of determination in the bomb calorimeter and in the Boys calorimeter is the difference between the final temperatures of the gases in the two cases, a determined calorific value being taken as referring to this temperature but 25°C being used as the reference

temperature for the reporting of results, so that, in general, a correction must be applied to the determined value. With the bomb calorimeter, the final temperature of the gases is the same as the temperature of the water in the vessel at the end of the chief period, and is about 27°C in the Griffin–B.C.R.A. Isothermal Calorimeter. In the Boys calorimeter, the temperature of the effluent gases is measured, and must be not more than 10°F greater than that of the inlet water: the actual value may be as low as 17°F. J. E. C. TOPPS[6] has calculated the temperature coefficients of the calorific values of butane and town gas to be percentage decreases of 0·0060 and 0·0094 (respectively) for each degree centigrade increase of temperature: even for the 10°C difference which is possible, the absolute effects are considered to be negligible.

Determination of the calorific value of town gas using a resistance thermometer
The authors' first experiments with town gas were made using the gas from the laboratory taps, but since this could not be assumed to be of constant calorific value a cylinder of coal gas was obtained and used in all later tests. A platinum resistance thermometer and Smith's Difference Bridge were used to measure the temperature rise (about 0·4°C). The first series of determinations gave irregular results, but this was found to be due to burning of the rubber sealing ring of the bomb. A steel collar was therefore fitted to the cap of the bomb to protect the ring; under these conditions good repeatability was obtained.

A series of five determinations under satisfactory conditions gave the following results.

> Gross calorific value at constant volume and 12 atm (gauge) pressure = 400·0 mean B.t.u./ft^3 measured at 60°F and 30 in of mercury, and saturated with water vapour.
> Standard deviation = 1·9 B.t.u./ft^3 = 0·48 per cent.

Conclusions
The volume of gas contained in a calorimetric bomb can be measured with high precision. With Calor gas the temperature rise is similar to that for a solid fuel and an ordinary bomb-calorimeter thermometer may be used; for town gas the temperature rise is much smaller and a resistance thermometer must be used to measure this with precision. The combustion is explosive so that certain precautions (which have been described) must be taken. Under these conditions the calorific value may be measured with a standard deviation of approximately 0·5 per cent.

It is desirable that the residual gases from tests under the conditions finally chosen should be examined using an infra-red spectrometer, standardized for carbon monoxide, to see whether combustion is complete, and similar tests should be applied to the exit gases from a Boys calorimeter. It is also desirable that a longer series of tests should be made to confirm the present observations and that gas from the same cylinder should be tested in a Boys calorimeter. A disadvantage of the Boys calorimeter is that it is not standardized with a gas of known calorific value. It seems possible that the bomb calorimeter (whose effective heat capacity is determined using standard benzoic acid) could be

used for an accurate determination of the calorific value of a cylinder of coal gas; this gas could then be used to calibrate Boys calorimeters, and so to remove the bias which might possibly exist and which would perhaps cause errors.

Since unpurified coke-oven gas, which is often used for heating coke ovens and other industrial furnaces, must be purified before its calorific value is determined in a flow calorimeter, the value so determined should be corrected to that of the unpurified gas for calculations of thermal efficiency. Unpurified gas could, however, be used in a bomb calorimeter, and the bomb washings would serve for a determination of sulphuric acid due to hydrogen sulphide in the gas. It also seems likely that, by saturating both the gas and the oxygen with water vapour before admission to a dry bomb, and subsequently collecting and measuring the water in the bomb after combustion, a more accurate estimate of the amount of liquid water produced (required for the calculation of the net calorific value) should be possible than when using a flow-type calorimeter.

HEAT OF IGNITION

In *B.S. 1016:* Part 5[1] it is stated (p 15): 'The heat release from the . . . firing wire is a source of constant heat gain provided that the quantity and quality of the . . . firing wire are kept the same for each determination. . . . The heat release from the firing wire is obtained from the weight of a piece of wire equal in length to the distance between the poles of the bomb, allowing 335* cal/g for nickel–chromium wire or 100 cal/g for platinum'. As noted in Part IV[7] of this series, M. KLIMOWA and B. G. SIMEK[8] reported the value of 335 cal/g of nickel–chromium wire; we have confirmed this value.

In each of our own observations ten pieces of wire, each 1·2 in. long, were used and the heat developed measured by a calorimetric determination in an isothermal calorimeter at equilibrium; as the temperature rise was small, the cooling correction was negligible. In three such determinations, the measured heat releases were 2·8, 2·3 and 3·6 cal. The mean, 2·9 cal, adjusted to a length of 1·35 in. (equivalent to 0·01 g for 36 s.w.g. nickel–chromium) gives a value of 0·33 cal/mg, which agrees with the reported value.

When a current is passed at a constant potential difference (V volts), the power developed is, for a cube of side 1 cm, V^2/R watts, where R is specific resistance (Ω cm). The heat released is $V^2t/4{\cdot}2R$ cal, where t is time (sec), and the theoretical temperature rise will be proportional to $V^2/Rc\rho$ (where c is specific heat, cal/g °C, and ρ is density, g/cm^3) for a given time of passage of current. It is convenient to use the known heat release per unit weight of nickel–chromium for the calculation of corresponding values for other materials (iron and platinum) from the ratios of the values of the effective potential difference, which will clearly vary as $(Rc\rho)^{\frac{1}{2}}$. The required characteristics of the three materials are given in *Table 2.*

We have $V_1 : V_2 : V_3 : : 3{\cdot}94 : 1{\cdot}19 : 1{\cdot}00$.

* Actually given incorrectly as '35'.

The power developed will vary as V^2/R, so that $P_1 : P_2 : P_3 : : 1{\cdot}55 : 1{\cdot}30 : 1{\cdot}00$. The amounts of energy released per unit weight for a given time of passage of current will therefore be:

$$E_1 : E_2 : E_3 : : 3{\cdot}90 : 3{\cdot}57 : 1{\cdot}00$$
$$: : 3{\cdot}35 : 3{\cdot}07 : 0{\cdot}86$$

The value for platinum is rounded in *B.S. 1016:* Part 5 to 1 cal per 0·01 g.

Table 2. Properties of materials used for firing wire

Material	*Specific resistance** R (Ωcm)	*Specific heat c* ($cal/g\,^\circ C$)	*Density* ρ (g/cm^3)
1. *Nickel–chromium*	110×10^{-6}	0·125	8·5
2. *Iron*	12×10^{-6}	0·112	7·8
3. *Platinum*	11×10^{-6}	0·032	21·4

* At 18° to 20°C.

When using 36 s.w.g. nickel–chromium wire on poles 1·5 in. apart (as in the Griffin–B.C.R.A. bomb), the heat release is 3·7 cal. When using the same length of 44 s.w.g. platinum wire, the heat release calculated on the above basis is only about 0·5 cal. If iron wire is used, in addition to the calculated heat release, it is necessary to allow for the thermal effects of the oxidation of the iron and the attack by acid vapours on unfused iron; for this reason, and because of the disfigurement of the bomb surface with fused globules, iron is not recommended.

The lower value for platinum than for nickel–chromium is of no importance, but it must be remembered that some uncertainty attaches to the value for platinum. The value for nickel–chromium (which breaks) is experimentally established, though it depends on a standard tautness of stretching between the poles which is readily obtainable. The value for platinum is based on the assumption that the period for which the circuit is closed is the same as when using nickel–chromium; in general, this will not be true, though the actual deviation may be small. This uncertainty with platinum, and the unique convenience of nickel–chromium, lead us to recommend the latter for general use.

NITRIC ACID CORRECTION

It will be recalled that, in Part IV[7], it was recommended that the nitric acid correction be considered as a constant, for a constant heat release in a particular bomb, for bituminous coals and most liquid fuels; *iso*pentane, coke and anthracite were exceptions, the former being too fast-burning and the two latter too slow-burning compared with the other fuels. It may be that, under the conditions recommended in Part X[9] for the combustion of anthracite and *iso*pentane, two of these exceptions will disappear, though this has not yet been checked experimentally. The statement made in *B.S. 1016:* Part 5 (p 21) that 'The nitric acid correction for coke is not constant and shall be determined each time a determination is carried out.' remains valid.

For the revision of the *Draft ISO Recommendation*[2] for the determination of the calorific value of coal, it has been agreed, on the recommendation of the Russian delegation, that the nitric acid correction be taken as $0{\cdot}0015Q$ (Q = heat release) for bituminous coals and $0{\cdot}0010Q$ for anthracites, irrespective of the capacity of the bomb (250 to 350 ml capacity, as in *B.S. 1016:* Part 5), the heat release being fixed at 7500 ± 1000 cal. In Part IV, for a bomb of 255 ml capacity, we showed that the nitrogen correction was $10{\cdot}2 \pm 1{\cdot}4$ cal for a heat release of 7500 cal from bituminous coal, benzoic acid, gas oil, benzene, gasoline and aviation spirit, which may be expressed as $0{\cdot}0014$ ($\pm 0{\cdot}0002$) Q and which is thus in accord with the Russian recommendation. For anthracite, the nitrogen correction was 6·7 cal, or $0{\cdot}00089\ Q$, which also is in reasonable accord with the Russian recommendation.

B.S. 1016: Part 5 requires the nitric acid correction to be ascertained in all determinations of effective heat capacity, but permits the same value to be applied in tests on coal. We consider that this remains the best practice, but it is clear that a value two thirds of that determined for benzoic acid can safely be applied in tests on anthracite under the combustion conditions recommended in *B.S. 1016:* Part 5. If it is possible to recommend a general rule for coke under the combustion conditions recommended in Part X (initial oxygen pressure 35 atm, gauge), this will be submitted later.

HIGH-PRESSURE BOMB

In *B.S. 1016:* Part 5 (p 23) our general recommendations as to the capacity, weight, thickness and materials of construction of the bomb have been accepted, the weight being limited to 3·25 kg. With the modified procedures now recommended (Part X) for liquid fuels, the margin of safety with our design is more than adequate for all conditions. The same design meets the requirements of *I.P. 12/58T*[3], so that the specification in this document of a system of remote firing should be dispensed with: it represents a fear which can now be exorcized.

Many operators accepted the offer[10] of the British Coke Research Association to test their bombs by the ringing test described in Part VI[11]. No further examples of defective bombs were found, and it now seems that the likelihood of defect is confined to bombs issued in the period 1927–40.

A development of the Griffin–B.C.R.A. bomb (essentially a B.C.R.A. bomb C: see Part V[12], Figure 8) not hitherto reported, enables it to be secured and opened by hand. Thus the convenience of the operator is further served and the disfigurement of bombs after numerous insertions into a bench stand prior to closing or opening with a spanner will not occur, so that a bomb should keep its showroom finish for a life of 20 years or more. Hand-tightening is made possible by the use of an O-seal, or elastomer ring of circular cross section, which is fitted into a step cut on the inner face of the top of the bomb cup; the O-seal (of synthetic rubber) is slightly oversize and therefore grips the wall of the step. The lower face of the bomb cap projects $\frac{1}{16}$ in. into the bomb below the level of the step and forms a flame trap of 0·0005 in. width. The O-seal projects 0·009 in. above the top of the bomb cap and hand-tightening of the union nut brings the rim of the bomb cap into contact with

the rubber. Further tightening (through one eighth of a turn) compresses the rubber and brings the rim of the cap into contact with the top of the cup; the rubber, pressing against the side of the bomb-cup step and the side of the projecting portion of the bomb cap, gives a seal which will withstand a gas pressure of at least 50 atm. The union nut is knurled to make it possible for it to be easily gripped, even in the small hand of a woman laboratory assistant.

TEMPERATURE MEASUREMENT

In Part IV[7] we drew attention to the fact that the inaccuracy of temperature measurement is the greatest source of error in routine bomb calorimetry. It seemed desirable that there should be available thermometers of a higher grade than those normally supplied to *B.S. 791:* 1954[13]. This recommendation has now been accepted by the committee concerned: in the future there should be available special-grade thermometers (of 6°C range) for which the average change of error for ten intervals of 0·5°C (the two extreme intervals of 0·5°C being excluded) should not exceed 0·004°C. Such thermometers should be further calibrated at 0·2°C intervals, or, for use with an isothermal calorimeter, at 0·2°C intervals over ranges of 0·5°C around the usual starting temperature and 1·0°C around the expected final temperature. It may be desirable to calibrate the thermometer at partial immersion, to the normal depth of immersion in the calorimeter.

In Part VIII[14] we reported that, using a platinum resistance thermometer and a Smith's Difference Bridge, the standard deviation of single determinations using benzoic acid had been reduced to 0·075 per cent, half the practical lower limit when using a mercury-in-glass thermometer. This improvement is due to the fact that, with the more refined system, the possible error of a single temperature measurement is only 0·0002°C. The actual temperature observations are made in ohms, but there is no need to convert to °C: if the effective heat capacity is recorded in cal/Ω, the result (Ω) of a determination of calorific value, multiplied by this effective heat capacity, gives the heat release in calories. It should be noted that a platinum resistance thermometer in a silver sheath gives shorter temperature-lags than does a mercury-in-glass thermometer, an advantage in determining such factors as T_m in the Dickinson cooling correction. The measurement of the resistance on a Smith's Difference Bridge is as quick and as convenient to the operator as the reading of a mercury-in-glass thermometer and involves less eye strain.

Whilst the use of a special-grade bomb-calorimeter thermometer may be adequate for most routine determinations of calorific value, a resistance thermometer and a Smith's Difference Bridge could well serve in a headquarters laboratory for special determinations and for the checking of bomb-calorimeter thermometers.

In *B.S. 1016:* Part 5 it is stated (p 25) that: 'The timer may be usefully fitted with a device so that audible warnings are emitted'. The audible warnings should be emitted for 10 sec at intervals of 1 min; they provide a signal to the operator, who should read the temperature at the end of the warning. During this period of 10 sec, the thermometer must be tapped lightly; this can be done manually, but it is preferable that the thermometer should be

tapped mechanically by a vibrator. In the authors' experience this not only eases the operator's task but also probably enhances the reliability of the indicated temperature: the average deviation of a series of consecutive values of the change in temperature per minute is less than when tapping with, say, a pencil.

On the Griffin–B.C.R.A. Isothermal Calorimeter, devices are fitted which act as timer and tapper. The thermometer is fitted with two rubber bungs, one of which closes the aperture in the top cover of the calorimeter vessel and the other of which supports the thermometer in a boss (fastened to the tube which almost encloses the thermometer for the jacket). This upper bung rests in double metal rings, screwed together; when the thermometer is approximately in position and facing the front, screwing of the outer ring raises the thermometer to the correct position for tapping.

The tapper is attached to the top of the jacket-thermometer tube and its actual position can be adjusted. The force of impact on the thermometer is adjustable, a stronger tap being required for solid-stem than for enclosed-scale thermometers. When correctly set for the particular type of thermometer, tapping with a pencil, after the mechanical tapping period, gives no change in in the indicated temperature. The audible warning system is built into the timer unit, and is synchronized with the tapper so that both operate for 10 sec before the completion of each period of 60 sec.

It is desirable to test each operator, to see whether, in reading a thermometer, he has an unconscious bias towards the selection of certain numbers for the third decimal place and the rejection of others. This can be done by noting the frequency of occurrence in the third decimal place (10^{-3}°C) of each of the numbers 0 to 9 for a large number of observations in which uni-

Table 3. Cooling corrections (°C) in 10 determinations

Test No.	*Regnault–Pfaundler*		*Dickinson*
	½ min	*1 min*	
198	0·0127	0·0132	0·0135
199	0·0003	0·0006	0·0012
200	0·0071	0·0071	0·0073
201	0·0071	0·0073	0·0073
204	0·0077	0·0079	0·0079
205	0·0161	0·0163	0·0164
208	0·0051	0·0053	0·0054
209	0·0108	0·0111	0·0109
210	0·0130	0·0132	0·0133
211	0·0042	0·0045	0·0046

form occurrence of all numbers could be expected. With one operator whom the authors tested, readings 0 to 3 were favoured; with another (less experienced) operator, favoured readings were 0, 2 and 8. A bias of this type can arise from an incorrect eye level, but where this does not apply, where there is a genuine unconscious bias, it can only be overcome by training.

Although it has been suggested that, for work of high accuracy, readings of temperature should be taken every 15 sec, this only applies when the temperature can be read to 0·0001 °C, as in the work of J. COOPS and K. VAN NES[15] on the calorific value of liquid hydrocarbons with a standard deviation of the order of 0·01 per cent. A claim that reading the temperature at intervals of ½ instead of 1 min, using a mercury-in-glass thermometer, would lead to higher accuracy was investigated. A series of 10 tests was made and the cooling corrections (Regnault–Pfaundler) calculated for readings at ½ min and 1 min intervals; the Dickinson correction was also calculated in each case. The results are recorded in *Table 3*.

It will be seen that, between the two estimates by the Regnault–Pfaundler formula, there are differences in the fourth decimal place which in only one case (Test 199) result in the values rounded to three places differing by 0·001 °C, to which difference, the accuracy of temperature measurement being what it is, no significance can be attached. The results also demonstrate the excellent agreement between the estimates obtained by the Regnault–Pfaundler and Dickinson formulae.

CRUCIBLES

In *B.S. 1016:* Part 5 (p 25), crucibles ⅝ to ¾ in. high and of 1 in. maximum diameter are recommended for coal, being made of 'platinum *or* nickel–chromium *or* silica' and suitable thicknesses being specified; for coke (p 19) the diameter is 1·5 in. The authors have always found a crucible made of nickel–chromium preferable to the equivalent silica version except for one purpose: it is only with a silica crucible with a pad of alumina that we have been able to obtain visually complete combustion of 1·0 g of natural graphite; with a nickel–chromium crucible, as recorded in Part I[16], 0·9 g could be burnt but 1·0 g left a smear of unburnt carbon. Generally speaking, under difficult conditions, such as in a bomb of small capacity, a silica crucible will give smears of carbon when a nickel–chromium crucible will give visually complete combustion.

It is now possible to buy nickel–chromium crucibles, made from spun sheet, with a flange for supporting the crucible in a ring secured by a screw to the non-insulated pole and this form is the most convenient to use. Our final recommendations as to crucible dimensions were made in Part X[9]; the only additional comment to be made concerns the use of B.D.H. thermochemical standard benzoic acid, and this is dealt with later in this paper.

It should be noted that platinum crucibles are unsuitable for use with coals of high iron content, the iron oxide fusing on the surface.

PRESSURE GAUGE

In *B.S. 1016:* Part 5, no dimensions are given for the pressure gauge, but gauges of 2·5 in. face diameter, as are often fitted, are too small; a gauge with least a 5 in. face should be used so that the initial pressure can be read easily to 1 atm, the units in which the gauge should be calibrated. Connection from the oxygen cylinder to the bomb should always be made with armoured rubber pipe.

BENZOIC ACID

In *B.S. 1016:* Part 5, the recommended procedure (p 27), after weighing 1·2 g of benzoic acid into a crucible, is: 'Place the crucible in an air-oven and heat at a temperature of 121° to 126°C for 1 hour . . . (Note 3).' Note 3 (p 28) says: 'Alternatively, pelleted benzoic acid may be exposed for at least 3 days in a desiccator containing concentrated sulphuric acid or magnesium perchlorate.' For the revision of the *Draft ISO Recommendation*, it has been agreed that desiccation and pelleting be recommended with a note to permit heating at 121° to 126°C for 1 hour as an alternative. In the 1942 edition of *B.S. 1016*, both procedures were permitted in the text (p 58), but in Fuel Research *Survey Paper No. 44*[17] (1940), only the melting procedure was advised (p 51). M. HISSINK and B. P. KNOL[18] advise the briquetting of benzoic acid which has been dried for two or three days over phosphorus pentoxide, and say that fusion is incorrect, as the formation of anhydride can be demonstrated after heating to 135°C, this being based on G. WADDINGTON's summary[19] of the work of F. W. SCHWAB and E. WICHERS[20].

As one of the present authors has already pointed out (R. A. MOTT[21]), there is, in fact, no reason to doubt that heating for 1 hour at a temperature not exceeding 126°C is satisfactory in giving fusion without decomposition, so that Hissink and Knol's objection to this method of combined drying and compacting is not valid. On the other hand, it would not surprise the authors if, in many laboratories, the fusion were carried out over a small flame: under these conditions the temperature might well exceed the safe limit of 126°C and decomposition would occur. If practised, fusion must be carried out in an oven which can be correctly regulated, with the benzoic acid adjacent to the thermostat. As adjustment to 126°C is difficult to achieve on many ovens, we fear that errors may have arisen through over-heating of the benzoic acid, leading to an incorrect value for the effective heat capacity of the calorimeter.

Desiccation and briquetting provide a far more convenient way of drying and compacting the benzoic acid, and are free from sources of error. When using powdered A. R. benzoic acid, it should be dried as specified in *B.S. 1016:* Part 5 (p 28) and then briquetted in a good press. A suitable briquette press requires a mould at least $\frac{3}{4}$ in. deep and of $\frac{1}{2}$ in. diameter, both it and the plunger being made of stainless steel. Two charges are usually necessary to obtain a briquette of 1·2 g. The briquette should be burnt in our crucible No. 1 (Part X[9], Table 5).

When using B.D.H. thermochemical standard benzoic acid, which is supplied as pellets of approximately 0·2 g each, drying should again be carried out by exposure to a powerful desiccant for at least three days. Then, if desired, a briquette can be made as with powdered benzoic acid. Alternatively, the dried pellets can be burnt without further compacting; for this purpose our crucible No. 6 (Part X, Table 5) should be used. As shown in Table 7 of Part X, the combustion characteristics, for the recommended initial oxygen pressure of 25 atm (gauge), are practically the same in this crucible as in No. 1, so that our recommendations as to suitable crucibles for various solid and liquid fuels are not invalidated.

Thus, with either powdered A. R. benzoic acid or B.D.H. pellets, the procedure of desiccation and (for powder) briquetting is much simpler than

the fusion technique: for this reason, as well as the elimination of the possibility of error through over-heating, the desiccation–briquetting procedure is to be preferred.

WEIGHING ERRORS

A method of assessing the 'precision' of balances, due to D. H. WARD[22], has been considered in connection with the determination of the calorific value of solid fuel. Ward's method has been applied to most of the balances in our laboratory, with various sets of weights, and the precision of weighing determined in each case. It has been shown that the potential accuracy of certain balances was vitiated by the use of sets of weights which were inadequate.

It is well known that, when determining a characteristic which is a small percentage of the fuel (moisture, ash, sulphur or nitrogen), it is unimportant to weigh the sample on a balance of the highest accuracy; however, for a characteristic which is a large percentage of the fuel (carbon or calorific value), this is not so. Quantitive estimates of these effects have been obtained and we recommend that the 1 g of coal or coke which is normally used for the determination of calorific value be weighed on the most accurate analytical balance available, using a good set of weights. Under such conditions, the weighing error which should not be exceeded more than once in twenty tests may be reduced to 0·25 mg, but without these precautions its value may be several times higher.

Under the recommended conditions, the possible error due to weighing-out the sample contributes little to the observed standard deviation. The calculations have confirmed that temperature measurement is the greatest source of error. The subject will be elaborated in a later paper from these laboratories on weighing errors and technique.

CONCLUSIONS

The authors of this series have emphasized on many occasions that accurate determination of calorific value requires identity of thermal conditions in the determination of effective heat capacity and of calorific value, when the effect of constant sources of heat gain or loss is eliminated. It is important to recognize that good reproducibility of results is an indication of high accuracy only if bias is absent. Bias can arise from many causes: we have acted as referees in a number of disagreements on calorific value between buyer and seller and have concluded that such disagreements are most likely to arise from an incorrect determination of effective heat capacity, the determination which is the essence of bomb calorimetry.

We have drawn attention to the need to ensure complete combustion of the benzoic acid, but it is often overlooked that, if combustion is incomplete, the temperature rise is too low for the certified calorific value, so that the calculated effective heat capacity is too high; this results in all determined calorific values based on this effective heat capacity being too high. Many observers, comparing the calorific values of coal tested by buyer and seller, have assumed that the higher of two values is more likely to be correct, as is the case with many directly determined characteristics; in fact, there are no grounds for making this assumption, unless there is a history of agreement

between the two laboratories, when the lower value may indicate incomplete combustion of the coal.

Since bias may arise in this way, good duplication may be misleading. We recommend as a useful test that A. R. benzoic acid be used to check the performance of calorimeters and operators. The powder, dried as recommended and prepared in pellets of approximately 1·2 g (weighed as recommended, the balance being read to 0·1 mg), should be burnt in our No. 1 crucible, set 4 in. below the bomb cap, using an initial oxygen pressure of 25 atm (gauge); six determinations should be made and the mean calorific value of benzoic acid, and standard deviation, calculated using the accepted value for the effective heat capacity of the system. The standard deviation should not exceed 0·15 per cent and the mean calorific value should agree with the true value (see Part III[23]) to within 10 cal/g. If either condition is not fulfilled, a systematic survey of the apparatus and procedure should be instituted.

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The British Coke Research Association,
Coke Research Centre,
Chesterfield, Derbyshire

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CORRECTIONS TO SERIES: 'STUDIES IN BOMB CALORIMETRY'

Since the publication of Part I in 1954, and during the publication of the subsequent parts, a few small errors have been observed in the text, and a change of address has also been made necessary. Corrections are as follows.

Part I, 1954, **33**, 452, *Table 4*: values of C and H for benzoic acid should be 68·8 and 4·95, respectively.

Part II, 1954, **33**, 466, last line: '0·4' should be '0/4'.

Part II, 1954, **33**, 475, line 2 of caption to *Figure 4*: 'cal/min' should be 'cal/ml'.

Part VI, 1956, **35**, 488, lines 3 to 5 should read: '*Additional tests*—Photographs of some of the specimens listed in *Table 2* are given in *Figure 4*. Microphotographs of polished and etched specimens taken from the bombs (as received) are shown in *Figures 5* and *6*. *Table 2* . . .'

Part VI, 1956, **35**, 516, Letter to the Editor: 'Testing of Calorimeter Bombs'. Alter address to read:

The British Coke Research Association,
Chemical and Physical Laboratory,
Wingerworth, Chesterfield, Derbyshire.

Part VII, 1957, **36**, 464, line 3: 'saturated vapour pressure of water' should be 'water content of saturated air'.

Part VII, 1957, **36**, 465, para. 2, line 5: 'cover in' should be 'cover for'.

Part VIII, 1958, **37**, 7, line 19: '3·4' should be on the same line as 'With 22 . . . . vessel', and '$M_S + M_B/4$(kg)' should be raised to form a general heading for '3·4' and '3·2'. The thin rule is not necessary.

Part VIII, 1958, **37**, 8, last line: 'short' should be deleted.

Part VIII, 1958, **37**, 11, line 3 from bottom: 'jacket' should be 'washer'.

Part IX, 1958, **37**, 371, para. 1, line 3: 'in fuel' should be 'in the fuel'.

Part IX, 1958, **37**, 375, line 8 from bottom: 'microburette' should be 'semi-microburette'.

Part IX, 1958, **37**, 376, lines 12 and 15: 'microburette' should be 'semi-microburette'.

Chemical Structure and Properties of Coal XXIII—Electron-spin Resonance of Vitrains

J. SMIDT and D. W. VAN KREVELEN

Using the technique of electron-spin resonance, the following quantities were measured in air and in vacuo *on a series of vitrains with 71·7 to 96·5 per cent carbon: spin-lattice relaxation time T_1, number of free radicals per gramme and the second moment S_2 of the absorption curve. Furthermore, during heating at the constant rate of 3°C/min* in vacuo *the number of free radicals and the value of the line width at half height $\Delta H_{\frac{1}{2}}$ were determined in the range 200° to 600°C, and the variation of T_1 with temperature was measured for one vitrain with 88·4 per cent carbon. At room temperature T_1 reaches a maximum value of about 10^{-4} s at about 86 per cent carbon. The variation of T_1 is explained from the size of the aromatic surface area and the porosity of the vitrains. The influence of evacuation on the number of free radicals per gramme and on the value of S_2 at room temperature becomes clear in the light of the T_1 values.*

The variation in the number of free radicals and $\Delta H_{\frac{1}{2}}$ during the coking process largely depends on whether or not the vitrain is liable to soften. In softening vitrains the number of free radicals has been found to remain constant with increasing temperature up to about 300°C, after which a slight decrease, accompanied by the disappearance of tar from the vitrain, sets in; beyond about 400°C a sharp increase is noted, followed by a decrease at 500° to 600°C. $\Delta H_{\frac{1}{2}}$ remains constant up to about 400°C, after which it decreases, to rise again at 500° to 600°C. In non-softening vitrains the number of free radicals decreases hardly or not at all with rising temperature; $\Delta H_{\frac{1}{2}}$, on the other hand, increases continuously. The temperatures at which variations occur in the number of free radicals appear to be closely related to the temperatures at which changes are observed in the value of $\Delta H_{\frac{1}{2}}$ and to characteristic temperatures in the swelling and degasification process. The whole complex of phenomena is explained on the basis of the current views about the coking process. The variation of T_1 with temperature confirms that during carbonization the aromatic rings become pericondensed.

IN 1954 D. J. E. INGRAM and co-workers[1] and J. UEBERSFELD[2] discovered the presence of free radicals in coal. Since then, these and other authors have published several papers on this subject, some of which will be referred to in this article. In the middle of 1957 a start was made in our laboratory with the systematic reproduction of the experiments performed by Ingram and Uebersfeld. Soon a few new data were disclosed[3,4]. In this article further results are described. For those conceptions from the field of electron-spin resonance which will come up for discussion below, such as the spin-lattice relaxation time T_1, the line width at half height of the resonance curve, $\Delta H_{\frac{1}{2}}$, and the saturation phenomenon, we refer, for example, to D. J. E. INGRAM[5] or to J. E. WERTZ[6], both of whom give a great many literature references.

COMPOSITION OF COALS USED; APPARATUS

The coals used most frequently were a series of hand-picked vitrains of high purity (to be considered as almost pure vitrinites). Their compositions are given in *Table 1*.

Table 1. Data of the vitrains

Origin	Ultimate analysis (m.m.f.) %					V.M. (d.a.f.) %
	C	H	O	N	S	
U.S.A.	71·7	4·9	22·6	0·8	0·4	46·2
Indonesia, Borneo, Berau	75·9	5·3	16·2	1·6	1·1	47·1
France, Lorraine, Faulquemont	80·2	4·9	13·4	1·2	0·6	41·9
Holland, Limburg, Maurits	85·8	5·3	5·3	2·1	1·1	31·0
Holland, Limburg, Maurits	86·9	5·2	4·6	2·0	1·3	27·0
Holland, Limburg, Emma	88·4	5·0	3·3	2·4	1·0	25·0
Holland, Limburg, Maurits	90·2	4·5	2·8	1·9	0·7	17·9
Holland, Limburg, Hendrik	91·4	4·3	2·8	1·0	0·5	13·1
Great Britain, S. Wales	93·7	3·4	1·8	1·2	0·7	8·0
U.S.A., Pennsylvania	95·1	2·1	1·9	1·1	0·7	6·0
France, Alpes	96·5	1·5	0·7	0·7	0·6	4·0

We measured the electron-spin resonance with a 3 cm spectrometer of our own design. The principal features of this spectrometer are:

(*1*) TE_{011} transmission resonance cavity as sample holder;

(*2*) visualization of absorption curve on an oscilloscope;

(*3*) recording of derivative of absorption curve by means of a phase-sensitive detector (modulation frequency 1 kc/s);

(*4*) possibility of measuring the h.f. power dissipated by the specimen at resonance;

(*5*) possibility of heating the specimen during measuring at an adjustable rate per minute, up to a maximum temperature of about 800°C.

MEASURING RESULTS

Measurements on vitrains at room temperature

(a) *T_1 as a function of carbon content*—Vitrains showing the saturation effect were investigated to see whether their saturation factor varies[2] in accordance with the equation

$$Z = 1/[1 + \tfrac{1}{4}\gamma^2 H_1^2 T_1 T_2] \quad \ldots . \quad [1]$$

where γ = gyromagnetic ratio, H_1 = amplitude of alternating magnetic field, T_1 = spin-lattice relaxation time, and T_2 = spin-spin relaxation time. To this end we varied the value of H_1 by means of a calibrated attenuator and measured the relative change of the output signal. The theoretical and experimental variations of Z proved to be in good agreement with each other, as can be seen from the example shown in *Figure 1*.

It also appeared that saturation caused inhomogeneous broadening of the resonance line. The saturation effect was studied on a number of vitrains, both in air and *in vacuo*. The latter term as used here, as well as in the cases dealt with later, denotes that the specimen was evacuated until the e.s.r. absorption signal did not show an appreciable change any more. The pressure over the specimen then varies between 10^{-6} and 4×10^{-4} mm of mercury. T_1 was calculated from the saturation data.

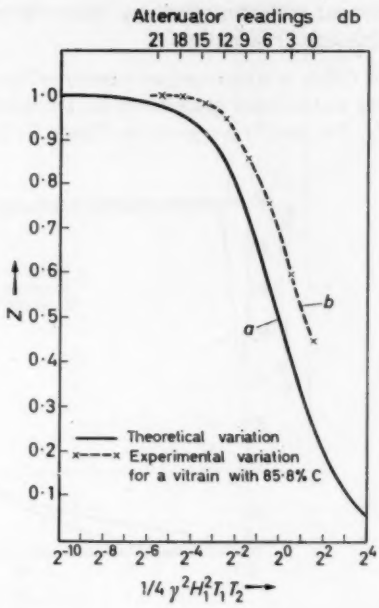

Figure 1. Variation of saturation factor Z

As the klystron available at the time of the measurements was of the low-power type, the lowest T_1 value that could still be measured was about 2 microseconds. The results, which proved to be independent of whether the vitrain was pulverized or not, are represented in *Figure 2*. Although the measuring points show a considerable spread, it can be clearly seen that both in air and *in vacuo* T_1 attains a maximum value at about 86 per cent carbon. In anthracites of very high carbon content no saturation, and hence no T_1, could be measured. The T_1 value of $1{\cdot}2 \times 10^{-7}$ measured on a Kussbassk anthracite by N. S. GARIF'YANOV and B. M. KOZYREV[7] seems to be in good

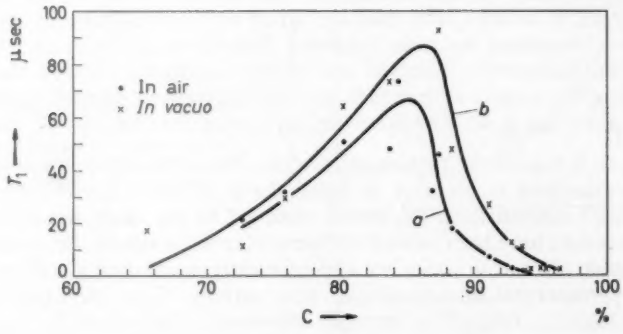

Figure 2. T_1 versus carbon percentage

agreement with these findings. Above 90 per cent of carbon T_1 increases very sharply upon evacuation.

(b) *Effect of evacuation on number of free radicals per gramme*—The number of free radicals per gramme of vitrain has been determined both *in vacuo* and in air. The results are given in *Figure 3*. Comparison of curves *a* and *b* shows

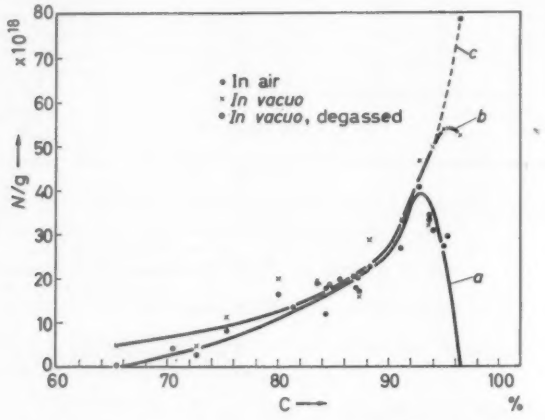

Figure 3. Number of free radicals per gramme versus carbon percentage

that at carbon contents above 94 per cent, the number of free radicals increases sharply upon evacuation (this was also observed by D. J. E. INGRAM[8]), and also at very low carbon percentages.

The course of curve *a* is in good qualitative agreement with the results reported by D. E. G. AUSTEN and D. J. E. INGRAM[9]. In the range between 70 and 90 per cent carbon, however, their results are systematically lower than ours. As this is the very region where vitrains tend to become easily saturated[3], the possibility that the saturation effect has led them astray should be taken into account. It is noteworthy that our values are about a factor of ten higher than those measured on coals from the Donetz basin by A. A. GALKIN and D. A. KICHIGIN[10]. None of our vitrain specimens showed the sharp decrease in the number of free radicals after pulverizing mentioned by N. S. GARIF'YANOV and B. M. KOZYREV[11] and by L. VAN GERVEN *et al.*[12].

(c) S_2 *as a function of carbon percentage*—The values of S_2 for a series of vitrains examined in air and *in vacuo* have all been derived by E. R. ANDREW's[13] method from the curves recorded by the phase-sensitive detector. The results have been plotted in *Figure 4* (curves *a* and *b*). The values of S_2 measured in air and *in vacuo* are approximately equal over a wide range of carbon percentages. Beyond 93 per cent carbon, $S_{2(\text{air})}$ increases rapidly, whereas $S_{2(\text{vacuo})}$ falls off to increase afterwards. The curves for S_2 closely resemble the corresponding curves for $\Delta H_{\frac{1}{2}}$, which are not given here.

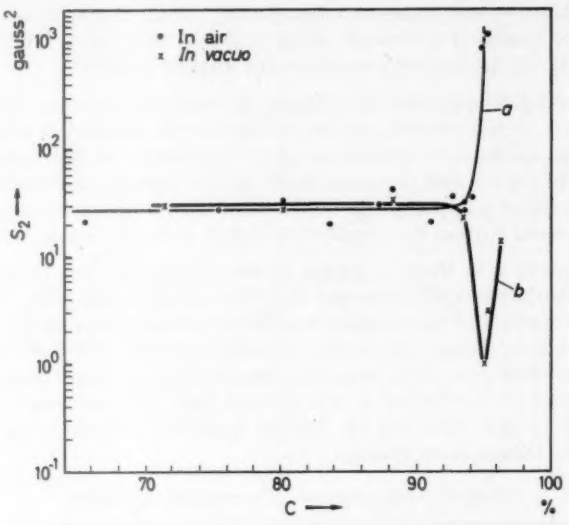

Figure 4. Second moment versus carbon percentage

Measurements on vitrains during carbonization

(a) *Number of free radicals as a function of temperature at different carbon contents*—Several vitrains, crushed to 300μ, were heated *in vacuo* from 200° to about 600°C, at the rate of 3°C/min. The temperature range is limited at the top by the conductivity of the vitrains which increases sharply in this region. This causes a rapid deterioration in the quality of the measuring cavity, which is used as a reference cavity for frequency stabilization, with the result that the recorded absorption signal becomes inaccurate. At regular time intervals we recorded the absorption curve by means of the phase-

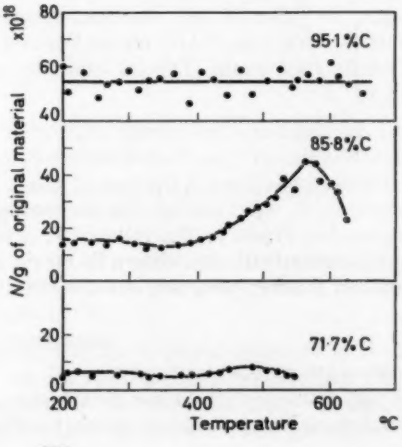

Figure 5. Number of free radicals per gramme of original material versus temperature for different percentages of carbon. Heating rate 3°C/min

sensitive detector and measured the quality of the cavity (the reciprocal value of the quality is a measure of the losses in the cavity). The number of free radicals was determined per gramme of original material.

The results fall apart into two clearly distinguished groups: at very high and very low carbon percentages the number of free radicals as a function of temperature is almost or entirely constant. The number of free radicals in the intermediate region first increases more or less sharply at higher temperatures, after which a decrease sets in. *Figure 5* shows typical examples of the two groups and further data appear in *Tables 2* and *4*, below.

Many curves also show a decline in the number of free radicals below 400°C. It could be clearly observed that this was attended with a release of tar-like components which largely reached completion around this temperature. For some vitrains the weight quantities of tar that have condensed against the colder part of the specimen tube and are no longer included in the determination of the number of free radicals have been compiled in *Table 2*. Also listed in this table are the weight quantities of the basic and final material and the final temperature.

Table 2. Weight quantities of some examined vitrains

Quantity	*Carbon percentages*							
	71·7	75·9	85·8	86·9	88·4	90·2	91·4	95·1
Wt of orig. material (mg)	75·8	56·3	69·2	29·8	72·9	40·2	38·0	38·7
Wt of final material (mg)	40	29	44	21	52	34	33	37·4
Wt of tar formed (mg)	9	9	15	3	13	4	2	0
Final temperature (°C)	570	540	630	600	610	600	630	660

(b) $\Delta H_{\frac{1}{2}}$ *as a function of temperature at various carbon percentages*—We also determined $\Delta H_{\frac{1}{2}}$ of the absorption curves obtained in the way described in the previous paragraph. Here again a clear distinction can be made between two groups: at very high (95·1 and 96·5) and very low (71·7 and 75·9) carbon percentages the value of $\Delta H_{\frac{1}{2}}$ increases steadily with temperature, whereas in the intermediate region $\Delta H_{\frac{1}{2}}$ remains constant at first, after which it falls off and finally rises again. Typical examples of the two groups are given in *Figure 6*.

(c) T_1 in vacuo *as a function of temperature*—For a vitrain with 88·4 per cent carbon the value of T_1 *in vacuo* has been determined as a function of temperature. Heating was done at the rate of about 5°C/min. The measurements for determining T_1 were carried out at constant temperature. The results are represented in *Figure 7*. The value of T_1 at room temperature proves to be in good agreement with that shown in *Figure 2* for the same vitrain. The sharp decrease of T_1 at temperatures above 400°C is striking.

DISCUSSION

Measurements at room temperature

(a) T_1 *as a function of carbon percentage*—Several investigators[14–21], when measuring on a sugar char *in vacuo*, noted that the specimens produced an

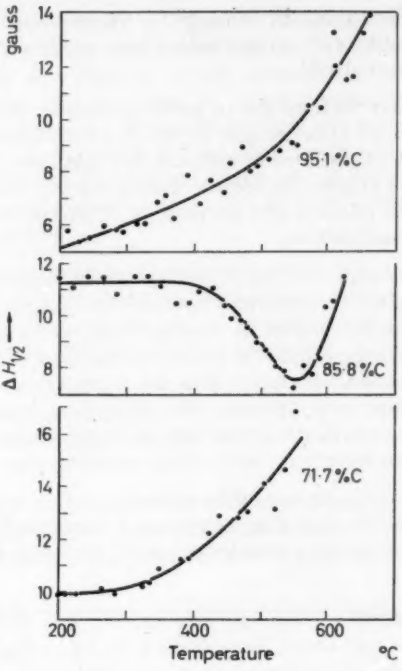

Figure 6. Line width $\Delta H_{\frac{1}{2}}$ versus temperature for different carbon percentages. Heating rate 3°C/min

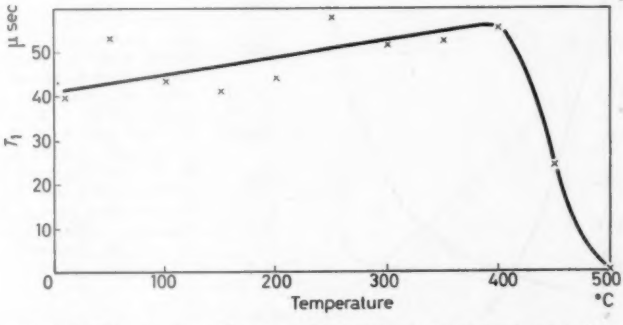

Figure 7. T_1 in vacuo as a function of temperature for a vitrain with 88·4 per cent carbon

e.s.r. signal which, upon admission of air, either vanished entirely or decreased in intensity. It was also found that of the gases present in air only oxygen can be responsible for the effect[16–18, 21].

This implies that oxygen interacts with the unpaired electrons in the char and consequently may act as an intermediate for establishing thermal equilibrium between the spin system of the unpaired electrons and their surroundings. It is obvious, therefore, that the amount of oxygen present has

an effect upon the value of T_1; the smaller the amount of oxygen the higher the value of T_1, as has indeed been qualitatively confirmed by measurements on sugar char[20].

These findings are in good agreement with our observation that vitrains examined *in vacuo* give higher T_1 values than the specimens measured in air (*Figure 2*), as well as with the fact that heating *in vacuo* causes T_1 to increase at first (*Figure 7*), because during heating small amounts of adsorbed oxygen will be released (the decrease of T_1 above 400°C shown in *Figure 7* will be discussed below).

The shape of the T_1 curves can be made plausible from the interaction between the unpaired electrons and oxygen. For the unpaired electrons T_1 will be the smaller as the chance of interacting with oxygen is greater, and this chance will be the greater as the vitrain is more porous. Assuming, as did Austen and Ingram[9], that the unpaired electrons are associated with the aromatic ring systems, the chance of interaction with oxygen will also increase with the size of the aromatic surface area, since unpaired electrons tend to move very easily along aromatic rings.

Data on the size of the aromatic surface area of vitrains have been reported by D. W. VAN KREVELEN and J. SCHUYER[22] and by P. B. HIRSCH[23]. Their results are represented in *Figure 8*. Although there are quantitative differences,

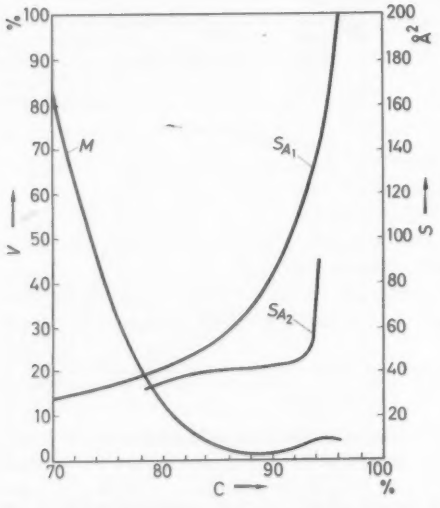

Figure 8. Aromatic surface area S_A and maximum inherent moisture content M versus carbon percentage, where M is based on measurements by J. A. DULHUNTY[24] *and* A. C. DUNNINGHAM[25], *S_{A_1} is due to* D. W. VAN KREVELEN *and* J. SCHUYER[22], *and S_{A_2} is based on the average layer diameters determined by* P. B. HIRSCH[23]

they display a distinct qualitative agreement in the same sense that the aromatic surface area shows little variation at low carbon contents and a marked enlargement at high carbon contents.

Quantitative data on the porosity of vitrains are scarce. Qualitative information can be derived from the maximum inherent moisture content, the variation of which, derived from measurements by J. A. DULHUNTY[24] and

A. C. DUNNINGHAM[25], has also been plotted in *Figure 8*. From this figure it can be seen that upon an increase in carbon content beyond 70 per cent the aromatic surface area increases only slightly at first, whereas the porosity decreases sharply. As a result, the value of T_1 must be expected to increase, as indeed it did. At carbon contents between 86 and 91 per cent the porosity is substantially constant, whereas the aromatic surface area increases in size. It is to be expected, therefore, that the decrease of T_1 will start in this region. This is in agreement with the experiments because the T_1 curve attains its maximum at about 86 per cent carbon.

Above 91 per cent carbon the aromatic surface area expands very rapidly, while the porosity in this region also increases slightly. Consequently, a sharp decrease of T_1 may be expected here, as has indeed been noted in the experiments. The qualitative variation of T_1 can thus be understood.

(b) *Effect of evacuation on the number of free radicals per gramme*—If evacuation should have any effect on the number of free radicals per gramme, then, in view of the foregoing, this should manifest itself in those vitrains for which T_1 has a low value.

The result of the experiment is in agreement with this expectation: in vitrains of high and of low carbon contents, oxygen causes unpaired electrons to disappear. (Ingram[8] also observed this phenomenon in some vitrains of high carbon content.)

Our results disagree completely with the findings reported by Singer and Spry[21] who, in measurements performed on a sugar char, noted that oxygen broadens the e.s.r. absorption line, but leaves the number of unpaired electrons unchanged.

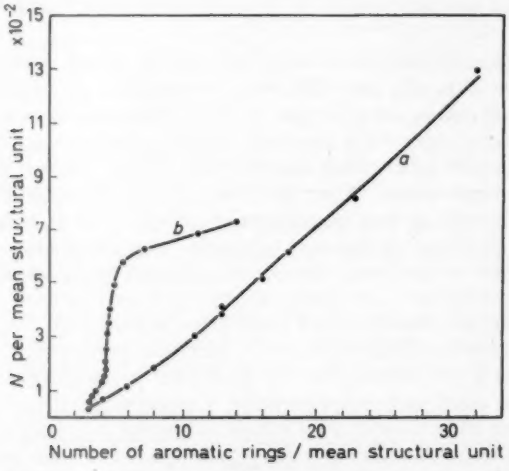

Figure 9. Number of free radicals/mean structural unit versus number of aromatic rings/mean structural unit: (a), in vacuo, using van Krevelen and Schuyer's data[22], and (b), in vacuo, using data due to Hirsch[23]

Using van Krevelen and Schuyer's[22] data on vitrains, one can rearrange curve *b* of *Figure 3* to give the number of free radicals per mean structural unit versus the number of aromatic rings per mean structural unit (*Figure 9*, curve *a*). Although the data for the vitrains are averages of widely scattered values, the relationship is surprisingly linear. This strongly supports Austen and Ingram's[9] view that the unpaired electrons are associated with the aromatic ring systems because a free radical will be stabilized the more easily by resonance as the aromatic complex is larger. Besides van Krevelen and Schuyer's data on the number of aromatic rings per mean structural unit, we have the disposal of Hirsch's[23] values for the average number of carbon atoms per layer as a function of the carbon content. We identified Hirsch's layers with van Krevelen and Schuyer's mean structural units and calculated the average between the possible numbers of cata- and peri-condensed aromatic rings consistent with the given number of carbon atoms per layer. In this way we found curve *b*, *Figure 9*. Although the number of free radicals per mean structural unit does go up with the number of aromatic rings, the relationship is much less linear than that found with van Krevelen and Schuyer's data. Furthermore, the very sharp increase in the number of free radicals per mean structural unit at about 4·5 aromatic rings per mean structural unit cannot be immediately understood.

Finally, it should be pointed out that the number of free radicals per mean structural unit may increase to fairly high values; *in vacuo* ratios as high as 1:8 have been measured.

(c) *S_2 as a function of carbon content*—In a previous publication[4] one of the present authors concluded from the course of S_2 for vitrains *in vacuo*, that at carbon contents below 93 per cent, the value of S_2 is a function of the dipolar interaction between the unpaired electrons and the protons of the cata-condensed aromatic rings. D. E. G. Austen *et al.*[26] reached a similar conclusion.

Further evidence of this view is the fact that at carbon contents below 93 per cent there is hardly any difference between the S_2 values of vitrains measured in air and *in vacuo* (*Figure 4*). The inhomogeneous broadening of the resonance line, observed in saturated vitrains, points in the same direction, as this phenomenon occurs when unresolved hyperfine structure plays a role[27]. At carbon contents above 93 per cent the value of S_2, measured in air, increases sharply with carbon percentage (*Figure 4*). This is because the line width is now no longer determined by dipolar interaction alone, but also by the short lifetime of the energy levels, characterized by T_1, which precisely in this region tends to very low values (*Figure 2*). That T_1 indeed starts to play a part here can also be concluded from other phenomena. For example, T_1 is strongly temperature-dependent[28]. Consequently, when S_2 is partially determined by T_1, it follows that S_2 must also be temperature-dependent. This has been confirmed experimentally. Furthermore, if the shape of the absorption line is exclusively determined by lifetime processes it assumes the character of the Lorentzian curve for which $S_2 = \infty$. It can be seen that at increasing carbon content S_2 rises to very high values, which does point to a growing influence of T_1.

For evacuated vitrains the values of S_2 are much lower in this region

(*Figure 4*). We pointed out that for evacuated vitrains with a very high carbon content, the value of S_2 is mainly a function of the dipole–dipole interaction between the unpaired electrons[4]; this statement conflicts with the view held by Austen *et al.*[26], who suppose that interaction of the unpaired electrons with electrons in the conduction band is the main cause of the line width.

Measurements during carbonization

(a) *Number of free radicals as a function of temperature at various carbon contents*—On the whole the numbers of free radicals at 200°C, present in the series of vitrains measured, were in good agreement with those found at room temperature (curve *b*, *Figure 3*), the only exception being the vitrain with 96·5 per cent carbon in which the number of free radicals has increased considerably at this higher temperature. The cause of the discrepancy must probably be sought in the fact that this particular vitrain is difficult to degas at room temperature. It follows therefore that the number of free radicals per gramme in properly degassed vitrains increases steadily with carbon content (curve *c*, *Figure 3*). This implies that the maximum in curve *a* of *Figure 9* would shift upwards at the same time.

It was pointed out above that the decrease in the number of free radicals below 400°C is accompanied by the disappearance of those tar-like vitrain components which, particularly below this temperature, condense against the colder portion of the specimen tube. It is worth mentioning that the weight percentage of tar formed and the percentage decrease in the number of free radicals in the majority of vitrains are of the same order of magnitude, as can be seen from *Table 3*. From this it can be concluded that, as far as the number

Table 3. Tar formation and decrease in number of free radicals below 400°C

Quantity	*Carbon percentage*							
	71·7	75·9	85·8	86·9	88·4	90·2	91·4	95·1
$\frac{\text{Wt of tar}}{\text{Wt orig. material}}$ (%)	12	16	22	10	18	4	3	0
Decrease in number of free radicals (%)	16	14	19	15	20	10	21	0

of free radicals is concerned, the tar produced and the initial material are identical; this provides a new indication that the tar molecules are the low molecular components of the coal.

As the temperature is raised further, the decrease in the number of free radicals is followed by an increase up to a maximum value N_m. *Table 4* shows the ratio between N_m and the number of free radicals, N_0, at the initial

Table 4. Maximum increase in number of free radicals

Nos. of free radicals	*Carbon percentage*									
	71·7	75·9	80·2	85·8	86·9	88·4	90·2	91·4	93·7	95·1	96·5
N_m/N_0	1·3	2·2	2·3	2·8	5·5	3·2	3·1	2·8	1·8	1·0	1·0

temperature for the vitrains examined. It is clear from this table that the increase in the number of free radicals is very slight at high and low carbon percentages and fairly sharp in the intermediate region, i.e. in the range where vitrain possesses caking properties.

This is in good agreement with the picture we are now able to form of the carbonization of coal, thanks *inter alia* to the knowledge gained from carbonization experiments with model substances (P. M. J. WOLFS *et al.*[29]). This picture can be outlined as follows. At about 400°C the C—C bonds of the bridge structures start losing their stability, with the result that in the temperature range between about 400° and 480°C a kind of depolymerization takes place in the coal. Naturally, this is attended with the formation of free radicals; at the same time disproportionation takes place: part of the fragments get saturated with hydrogen withdrawn from other fragments. The former evaporate as tar, whereas the latter condense to yield semicoke with large aromatic clusters. Upon heating to about 500°C or above the so-called secondary degasification sets in. During this stage peripheral hydrogen is released by thermal effects which also give rise to further condensation. At lower carbon percentages depolymerization is largely obscured by another reaction in which OH groups of the one molecule react with H atoms of the same or another molecule. This also causes condensation to larger units, be it without formation of additional free radicals. At very high carbon contents the aromatic system is so extensive that there exists already a very high degree of thermal stability. Heating no longer produces any tar and it will be understandable, therefore, that the number of free radicals should remain practically constant.

From the foregoing it will also be clear now that in all vitrains showing a distinct increase in the number of free radicals with rising temperature, this increase is followed by a decrease; for during the combination of aromatic complexes free radicals will easily get lost, this being in agreement with a general statement by Austen *et al.*[26].

It only remains to be considered now whether the decrease in the number of free radicals is a real one. One might imagine that owing to the fall in weight, caused by the formation of tar, the concentration of free radicals in the residue would actually increase. However, from a comparison of the weight losses as a function of temperature and time it can be derived that this is not so.

(b) $\Delta H_{\frac{1}{2}}$ *as a function of temperature at different carbon percentages*—It has been mentioned above that at low values of T_1 the line width becomes temperature-dependent. This statement is supported by the observation that S_2 for vitrains of the highest carbon contents increases with temperature. The increase will be the stronger as T_1 is smaller. In this respect the slopes at 71·7, 75·9, 95·1 and 96·5 per cent carbon—all of which bear the same character (see *Figure 6*)—were in good qualitative agreement with the corresponding T_1 values in *Figure 2*, curve *b*; for the slopes of the curves at 75·9 and 95·1 per cent carbon were smaller than those at 71·7 and 96·5 per cent carbon.

In the intermediate range the value of T_1 is so high that $\Delta H_{\frac{1}{2}}$ is at first not temperature-dependent. At about 400°C, however, $\Delta H_{\frac{1}{2}}$ starts falling off with

increasing temperature. *Table 5* shows the values of $T_{\Delta d}$, the temperature at which ΔH_i decreases; T_{Ni}, the temperature at which the number of free radicals increases, and T_s, the temperature at which the vitrains start softening.

Although the values of $T_{\Delta d}$ and T_{Ni} can only be indicated approximately by the weak slopes of the corresponding curves and T_s is an average value, there still exists a distinct relationship between the three temperatures. This is indeed to be expected from the foregoing, for the number of free radicals will increase as soon as the softening process sets in. The attendant pericondensation causes narrowing of the line width[4]. The occurrence of pericondensation can also be clearly seen from the sharp decrease of T_1, which for vitrains with 88·4 per cent carbon starts at 400°C (*Figure 8*) and which we believe to be due to the capacity of the free radicals to move over a larger surface area and hence to get more easily into contact with conduction electrons, whose number increases with temperature (suggestion of Austen *et al.*[26]), or perhaps also with traces of oxygen. This increase of T_1 is insufficient at first to cause line broadening. At a higher temperature, ($T_{\Delta i}$), however, T_1 becomes so small that ΔH_i starts to increase.

Table 5. Characteristic temperatures of vitrains (symbols as in text)

Quantity	*Carbon percentages*					
	80·2	85·8	86·9	88·4	90·2	91·4
$T_{\Delta d}$ (°C)	360	380	380	400	460	460
T_{Ni} (°C)	360	380	380	400	430	450
T_s (°C)	350	360	365	385	460	—
$T_{\Delta i}$ (°C)	490	550	540	570	570	580
T_{Nd} (°C)	480	570	570	580	560	590
T_c (°C)	540	580	570	560	560	590
T_{frm} (°C)	420	500	520	500	500	560
T_{dgm} (°C)	430	460	470	480	500	540

According to the data in *Table 5* there exists a distinct relationship between $T_{\Delta i}$, T_{Nd}, the temperature at which the number of free radicals starts decreasing and T_c, the temperature at which the quality of the resonant cavity starts deteriorating owing to the growing conduction capacity of the vitrains. We defined T_c as the temperature at which the quality of the cavity decreases by one per cent per centigrade degree relative to its original value. The small difference between T_{Nd} and T_c confirms the above assumption that the ultimate decrease in the number of free radicals is caused by the union of aromatic complexes.

Finally, *Table 5* gives the values of T_{dgm}, the temperature at which the rate of degasification is maximum and T_{frm}, the temperature at which the increase in the number of free radicals is maximum. Although the value of T_{frm} can only be roughly approximated, the two temperatures are distinctly related, as was indeed to be expected.

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Centraal Laboratorium,
Staatsmijnen in Limburg,
Geleen, The Netherlands

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Ultra-violet–Visible Spectrum and the Aromaticity of Coal

R. A. FRIEDEL and J. A. QUEISER

The quantitative data previously reported for the visible spectrum of thin sections of Pittsburgh vitrain have been extended to 3000 Å in the ultra-violet region. Intensity values from 3000 to 2100 Å are obtained through extension of the spectrum by means of potassium bromide pellet spectra. The lone coal band, near 2650 Å, is typical of chars of oxygenated compounds and is found in the spectra of aliphatic α-hydroxy, conjugated carbonyl structures. These materials also produce the same intense 6·2 micron infra-red band found for coals and chars. Only small amounts of these chelating structures need be present. The relatively low spectral intensities of vitrain are compared with the high intensities of various polynuclear condensed aromatic compounds and hypothetical mixtures. Maximum allowable contents of these in vitrain are shown to be 2 to 13 per cent. Somewhat higher maximum contents, 25 per cent, are obtained from the comparison of areas under absorption curves of various polynuclear condensed aromatics with the area under the absorption curve of 84 per cent carbon vitrain, uncorrected for scattering or absorption by other species. These maximum allowable contents are appreciably lower than the amounts indicated by other methods. The colour of coal is not necessarily due to polynuclear condensed aromatics but rather may be attributed to small concentrations of free radicals, aliphatic or aromatic. Fine structure and strong specific absorption should occur at short wavelengths according to present X-ray data which limit the ring sizes to small polynuclear aromatics that have their strongest absorption bands in a comparatively small wavelength region; but no such region of strong absorption appears. Rather, the principal structures in 84 per cent carbon coal may be benzenoid and/or alicyclic with many quaternary carbons in diamond-like structures.

THE hypothesis of the polynuclear condensed aromatic structure of coal has been questioned on the basis of the ultra-violet (u.v.)–visible spectrum of vitrain from coal containing 84 per cent carbon[1]. The spectra shown in *Figure 1* were obtained on a thin section and potassium bromide pellets of 84 per cent carbon vitrain. For a thin section of Pittsburgh vitrain the quantitative absorption intensities (expressed as specific extinction coefficients, K, in litres/g.cm) at two wavelengths in the visible spectrum have been shown to be small compared with the absorption intensities of the most intense bands of several aromatic compounds and conjugated polyenes[1]. As one example, a quantitative calculation for the 9-ring compound violanthrene, showed that only 2·8 per cent of this substance could be present in Pittsburgh vitrain; in citing this single example it was pointed out that other polynuclear aromatic compounds absorbing in different regions of the spectrum could also be present. Calculations have been extended to determine concentration limits of other polynuclear condensed aromatic structures.

In addition to the method based on the most intense absorption bands, possible concentrations of polynuclear condensed aromatics in vitrain can also be determined by comparing total areas of absorption, i.e. the area under the absorption curves. It has been predicted that the latter method would produce greater values for possible concentrations of polynuclear condensed aromatics[1].

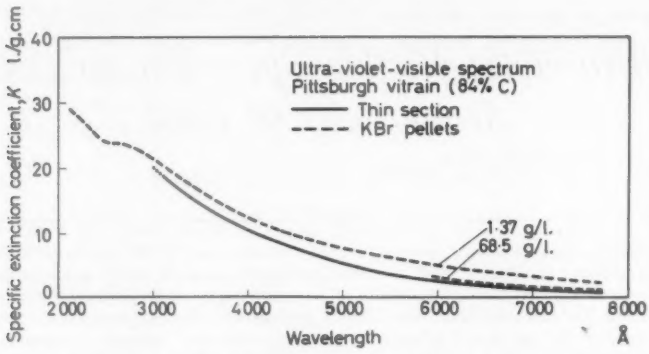


Figure 1. Spectra of Pittsburgh vitrain, thin section and potassium bromide pellets

The application of area measurements had to await quantitative measurements throughout the near-u.v. region.

Aliphatic structures rather than polynuclear condensed aromatics are thought to be of greater importance in the structure of coal. By the present work we are attempting to show that the latter may be present only in small amounts. Polynuclear condensed aromatics are not necessary for the explanation of the colour of coal. Colour can be attributed in large measure to small concentrations of free radical structures, which may be aliphatic or aromatic. As for the remaining structures in coal one of the principal objections to the assignment of aliphatic or alicyclic structures has been the carbon: hydrogen ratio. A ratio of over one can easily be achieved by assuming the presence of many tetrahedral C—C bonds in 3-dimensional or diamond-like structures. Such structures must be quite irregular as any appreciable regularity would be detectable by x-ray diffraction and other means. A high molecular weight coal 'molecule' may consist of many of these structures bonded together. No direct spectroscopic evidence of such structures has been found. However, the most important absorption characteristics in both u.v.–visible and infra-red (i.r.) spectra of coal can be attributed to aliphatic structures.

EXPERIMENTAL

Thin sections of vitrains were mounted on pieces of optical quartz by means of an adhesive—Lakeside 70 or marine glue. Small portions of the section that were free of holes and mineral occlusions were masked off for the measurements. Mechanical determinations of thickness were made by various methods: micrometer measurement of xylene-washed pieces of the section removed by melting the adhesive and sliding the section on to glass; determinations of weight and area of a removed section or portion of it; and measurements by a Leitz Tolimeter before and after a section is chipped off the adhesive. For 10 micron sections all of these methods are accurate to within $\pm 0{\cdot}5$ micron. The 10 micron sections are uniform in thickness, but the sections thinner than 5 microns vary in thickness so that only average values can be obtained.

The most accurate thickness determination has been the method based on absorbances (optical densities). A thick section, 20 microns, is measured to within $\pm 0{\cdot}5$ micron by a micrometer or Tolimeter and its absorbance density is measured at a given wavelength. Reflectance measurements are made at this wavelength and corrections are made to the absorbance for reflection losses. Then the absorbances of very thin sections, corrected for reflection losses, are used to calculate the optical thickness of these sections. This method is considered more accurate than those which measure mechanical thickness, as the optical thickness is independent of variations in thickness and of inhomogeneities such as submicroscopic holes.

Potassium bromide pellets were prepared by placing the sample, potassium bromide and two stainless-steel or agate balls in a stainless-steel or agate capsule mounted on a motor-driven vibrating arm. The balls strike the ends of the capsule 60 times per second. Pressing of 0·5 in. diameter pellets, about 0·5 mm thick, was done in an evacuable die at 20 000 lb thrust. Concentrations are expressed in the same units as solutions, that is, grammes of sample per litre of potassium bromide plus sample.

Table 1. Ultimate analyses

Material	*M.A.F. composition, weight per cent*				
	C	H	N	S	O (*diff.*)
Vitrain, Bruceton high-volatile A Pittsburgh seam	83·7	5·3	1·6	0·8	8·6
Vitrain, Velva lignite	71·9	5·3	0·7	0·6	21·5
Pitch, Koppers M.P. 80° to 85°C	91·7	4·7	1·2	0·5	1·9
Asphaltene, from 400°C hydrogenation of Pittsburgh seam coal	86·7	7·3	1·4	0·5	3·9

The curve in *Figure 1* for 68·5 g/l. nearly matches the spectrum of the thin section, but this concentration is too high to permit measurements below 6 000 Å. The curve for 1·37 g/l. lies above the curve for the thin section, as the apparent absorption includes an appreciable percentage of scattering.

A Cary Model 11 spectrophotometer was used in this work.

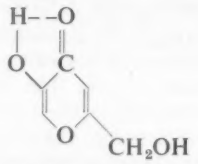
Ultimate analyses of samples are given in *Table 1*.

RESULTS AND DISCUSSION

Ultra-violet–visible and infra-red spectra

The u.v.–visible spectrum of Bruceton coal vitrain, 84 per cent carbon, is nearly devoid of spectral structure[1]. Absorption increases gradually from almost zero at the edge of the i.r. region (below 2·0 microns), through the visible and through the near-u.v. region to 2 100 Å. The only spectral structure found is a broad band shoulder near 2 650 Å. The same band has been found to exist in a great many coal derivatives as well as in chars prepared from oxygen-containing compounds. The i.r. spectra of these materials often differ but the strong 6·2 micron band invariably occurs; this band has already been

attributed to aliphatic hydrogen-bonded, conjugated carbonyls[2] as in the α-hydroxy pyrone, kojic acid,



Also, the u.v. spectra of this and similar compounds show their only band to be near 2650 Å, the location of the coal absorption band. Other aliphatic structures such as β-diketones also show their strongest i.r. and u.v. absorption bands in the same spectral regions as the 6·2 micron and 2650 Å coal bands. These chelate structures are very intense absorbers; only small amounts would be needed to produce the typical coal bands.

Aromaticity. Calculation of possible 5- and 6-ring aromatic structures

The results of statistical analyses[3] and, until recently, of x-ray determinations[4] on 84 per cent carbon vitrain have indicated that the vitrain consists of over 80 to 85 per cent aromatic structures, with an average of 5 to 6 aromatic rings. Concerning our previous calculation of the possible content of violanthrene in coal, van Krevelen has suggested that the *K*s (specific extinction coefficients) of 5- to 6-ring aromatics rather than of a 9-ring polynuclear condensed aromatic should be compared with the *K*s of this vitrain[2]. A comparison of *K*s in the u.v. region for a group of 5- and 6-ring polynuclear condensed aromatic hydrocarbons in dilute solution has been made with *K*s found for vitrain thin sections. *K*s for vitrain thin sections have been obtained down to 3000 Å; corrections have been made for absorption of the adhesive, which becomes appreciable below 3400 Å and is prohibitive below 3000 Å.

In *Table 2* the *K*s of Pittsburgh vitrain are compared with the average *K* for the most intense band for 27 5-ring compounds and for 20 6-ring compounds. Differences in *K*s are large; the possible concentration of mixtures

Table 2. Specific extinction coefficients of Pittsburgh vitrain and of polynuclear condensed aromatics with 5 and 6 rings

Material	*Wavelength, Å*	*Specific extinction coefficient K, l./g.cm*	*Max. wt % in 84% C vitrain*	*Quantitative comparison at 3050 Å*	
				K, av.	*Max. wt % of these aromatics in vitrain*
Coal: 84% C *vitrain*	3500 3000	15 20		19	
Polynuclear condensed aromatics, in dilute solution:					
5-ring compounds (27):					
Band maxima from	3500 *to* 2900	236 (*av.*)	$\frac{20}{236} = 8{\cdot}5$		
6-ring compounds (20):				143	
Band maxima from	3260 *to* 2910	337 (*av.*)	$\frac{20}{337} = 6{\cdot}0$	144	$\frac{19}{143} = 13$

of these 5- and 6-ring compounds in Pittsburgh vitrain should be 8·5 and 6·0 per cent respectively. A more direct quantitative comparison was made by determining the average K at a certain wavelength, 3050 Å, for all of the 5- and 6-ring compounds and comparing this average with the K of vitrain at the same wavelength. For a mixture containing equal amounts of all 47 of the 5- and 6-ring polynuclear condensed aromatics, the maximum possible percentage of such a mixture that could be present is 13 per cent. The compounds used in these determinations include a large number of benzfluorene-type compounds containing one 5-membered non-aromatic ring. The Ks of these are appreciably less than Ks of compounds consisting entirely of 6-membered aromatic rings. The K of Pittsburgh vitrain therefore would allow a somewhat greater concentration of benzfluorene types than of the intensely absorbing acene types.

Calculation of possible 2-ring and higher polynuclear condensed aromatic structures

To calculate possible concentrations of naphthalenes, the smallest polynuclear condensed aromatic system, it is necessary to obtain quantitative data as low as 2 100 Å. The use of potassium bromide pellets in measuring the near-u.v. spectrum of Pittsburgh vitrain below 3000 Å is open to two serious objections: (*1*) false absorption due to scattering of radiation by sample particles; (*2*) insufficient absorption due to insufficient reduction of particle sizes. In the first instance radiation losses due to scattering will produce an apparent increase in the absorption of the sample; in the second, the number of particles is too small to intercept the incident radiation efficiently, so that an apparent decrease in absorption results. Grinding alone does not yield particle sizes small enough to remove these two sources of error in u.v. spectra. The error due to inefficient absorption is worst for strongly absorbing substances; even for more weakly absorbing substances, such as vitrain from bituminous coal, it cannot be reduced enough to obtain reliable absolute absorption spectra of potassium bromide pellets.

A balance can be obtained between these two opposing errors for a band-free spectrum, such as that of vitrain, by an appropriate choice of grinding conditions. The absorption spectrum of a vitrain thin section from 3000 to 7750 Å can thus be closely paralleled by the spectrum of a potassium bromide pellet of the same vitrain (see *Figure 1*; grinding time, 4 hours). A reliable extension of the data to 2 100 Å can be made by means of the spectrum of the potassium bromide pellet[5]. Such an extension would be in error if the vitrain spectrum should undergo a sharp increase or decrease in absorption. No such sharp change occurs.

The potassium bromide pellet spectrum would indicate any sharp change in the absorption curve, at least qualitatively. This premise was investigated by comparing complete spectra of solids and solutions of soluble substances. Experiments on coal-derived asphaltene and coal tar pitch were carried out to determine whether the potassium bromide pellet spectra of these materials can parallel the spectra of solutions or thin films of the same materials over the entire spectrum. Spectra of asphaltene and coal tar pitch solutions were determined (*Figures 2* and *3*). By proper choice of grinding conditions,

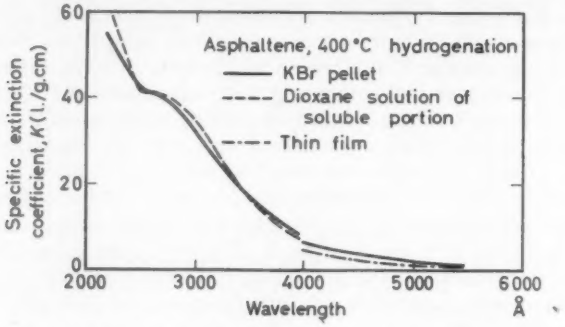


Figure 2. Comparison of u.v.–visible spectra of solution, film and potassium bromide pellets

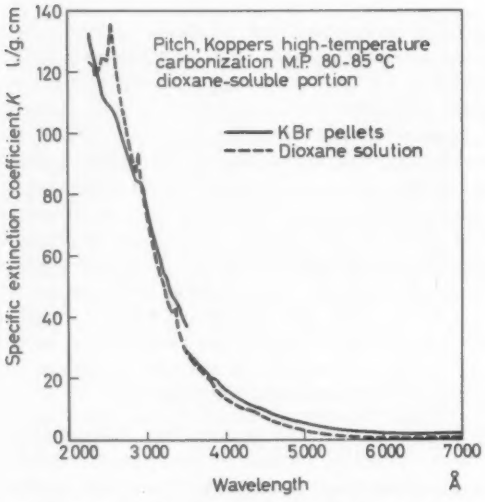


Figure 3. Comparison of u.v.–visible spectra of solution and potassium bromide pellets

potassium bromide pellets of these same materials (whole pitch and asphaltene gave pellet spectra identical to those of the dioxane-soluble portions) were prepared to match the solution spectra at the longer wavelengths. The spectra were then found to match at the short wavelengths. Inflections in the potassium bromide pellet spectrum of pitch indicate the rapid absorption increases and decreases (fine structure) of the solution spectrum. The existence of these fine-structure inflections in the spectrum of the pitch–potassium bromide pellet gives additional credence to the belief that vitrain spectra actually possess no fine structure.

In another experiment a potassium bromide pellet was prepared of a mixture of 10 per cent phenanthrene in 90 per cent vitrain to determine if the

spectrum of solid phenanthrene would be discernible in a spectrum of vitrain. *Figure 4* illustrates that all of the principal bands of phenanthrene are recognizable, although they are broader than in solution spectra. The spectrum of small crystals of phenanthrene alone consists of wide bands, such as those in *Figure 4*. If phenanthrene were present in coal as a solid solution in an

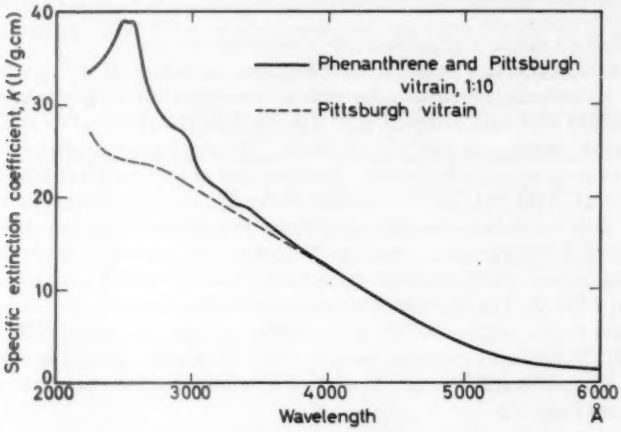


Figure 4. Demonstration of u.v. absorption of 1 part phenanthrene in the presence of 9 parts Pittsburgh vitrain. Potassium bromide pellets of Pittsburgh vitrain (0·056 cm thick, 1·38 g/l.) and phenanthrene plus vitrain (0·054 cm thick, 1·38 g/l. total)

amount of the order of 10 per cent, absorption bands in potassium bromide pellet spectra similar to or sharper than those shown in *Figure 4* would be anticipated; the absorption bands in thin section spectra would be as sharp or sharper than the narrow absorption bands found in spectra of liquid solutions[6–9].

*K*s in the u.v. region obtained by extrapolation are used in *Table 3* to calculate maximum possible percentages of polynuclear condensed aromatic

Table 3. Specific extinction coefficients of 84 per cent carbon vitrain and of polynuclear aromatic compounds at short wavelengths in the u.v. Calculation of maximum possible concentrations in vitrain

Material	*Wavelength Å*	*K in l./g.cm*			*Max. poss. conc. in vitrain, max. wt %*
		Compound (soln)		*Vitrain (K Br pellet)*	
		Orig.	*Corr.**		
Anthracene†	2534	1160	1230	24	2·0
Phenanthrene†	2520	393	416	24	5·8
Naphthalene‡	2220	762	813	28	3·4
Fluorenone†	2574	498	521	24	4·6

* Corrected for atoms that are not part of the chromophoric systems, namely hydrogen atoms. Oxygen in fluorenone is part of the chromophoric system, so no correction is made for the oxygen atom.

† In *cyclo*hexane solution. ‡ In 95 per cent ethanol solution.

compounds in vitrain at wavelengths of maximum absorption. Percentages are small in all instances. The values are not additive, as each compound has spectral absorption at the wavelength position of each of the other compounds. *K*s of these compounds, or of their alkyl or oxygenated derivatives, must be corrected for the percentage of non-chromophoric atoms to obtain concentrations in terms of aromaticity.

van Krevelen's mixture of polynuclear condensed aromatics

D. W. VAN KREVELEN *et al.* determined the spectrum of a 23-component mixture of polynuclear aromatics with an average of 4 rings per molecule[3]. They showed that this complex aromatic mixture did not absorb as intensely as two pitch samples in solution. However, the absorption intensity of 84 per cent carbon vitrain is considerably less than that of these pitch solutions (K = 76 and 91 at 3000 Å); also the spectra of the pitches were determined only to 3000 Å. Below this wavelength, absorption intensities of neither vitrain nor pitch increase appreciably; but the 23-component aromatic mixture shows the characteristic sharp increase in intensity below 3000 Å and reaches a K of 210 at 2520 Å. The maximum percentage of this kind of aromatic mixture that could be present in 84 per cent carbon vitrain was calculated to be 11 (*Table 4*). This shows good agreement with the above calculation of 13 per cent for a hypothetical mixture of 47 5-ring and 6-ring polynuclear condensed aromatics (*Table 2*).

Table 4. Specific extinction coefficients of 84 per cent carbon vitrain and of van Krevelen's 23-component mixture of polynuclear aromatics. Calculation of maximum total concentration of polynuclear aromatics in vitrain

Material	*K in l./g.cm wavelength, 2520 Å*
Pittsburgh vitrain, 84 per cent carbon	24
van Krevelen's mixture of 23 aromatic compounds	210
Maximum total concentration, weight per cent	11

In answer to the spectral results of D. W. VAN KREVELEN *et al.*[3] and of J. SHANNON[10], the spectra of neither pitch solutions nor extract solutions can be accepted as substitutes for coal spectra. Varying concentrations of these solutions give spectra with widely varying *K*s; Beer's law is not obeyed, perhaps because of free radicals produced by dilution[11]. Films of pitches or extracts constitute a more valid comparison with coal; the *K*s for films of coal hydrogenation asphaltene are lower than those of the corresponding solutions, which are known to contain more free radicals than the solid asphaltene[11].

Absorption areas

Quantitative determination of possible concentrations of polynuclear condensed aromatics may be carried out by comparing integrated areas under

absorption curves (equal to oscillator strengths divided by molecule weight) plotted as K_ν versus wave numbers. The measurement of absorption areas was made for 84 per cent carbon vitrain and for a group of compounds. The ratio of absorption areas of vitrain and each compound gives the maximum possible percentage of that compound, if the unlikely assumption is made that all of the area under the vitrain curve is due to the compound. The percentage values given in *Table 5* are still appreciably less than the 80 to 85 per cent

Table 5. Absorption areas under u.v.–visible spectra of solutions of polynuclear condensed aromatic compounds; calculation of maximum allowable concentration in vitrain from the absorption area (uncorrected) of 84 per cent carbon vitrain

Compound	*Absorption area,* $\int K_\nu \, d\nu$ *l./g.cm²*	*Max. poss. conc. in 84 per cent carbon vitrain, max. wt per cent*
Coal vitrain, 84 per cent carbon	0·00235*	
Naphthalene	0·0102	23
Tetradecahydrocoronene	0·0120	20
1,2′-Dinaphthyl	0·0110	21
2-(1′-Naphthyl)-1-Naphthol	0·0103	23
Anthracene	0·0113	21
Phenanthrene	0·0088	28
1,4-Chrysenequinone	0·0084	28
Pyrene	0·0076	31
Chrysene	0·0097	24
6-Hydroxychrysene	0·0094	25
1,2-Benzanthracene	0·0090	26
Naphthacene	0·0095	25
1,2,5,6-Dibenzofluorene	0·0082	29
Violanthrene	0·0099	24
		Av. 25
14-component mixture, equal weights		25

* Uncorrected for reflection losses, light-scattering by vitrain, or absorption by benzenoid structures, non-aromatics and free radicals.

polynuclear condensed aromatic concentrations supposedly present in 84 per cent carbon vitrain. Areas under the compound curves do not differ greatly, in spite of the wide range of structures, 2 to 9 rings. Thus approximately the same maximum concentration of total polynuclear condensed aromatics would be obtained for almost any combination of these compounds.

In calculating maximum possible concentrations based on areas, the values obtained are subject to appreciable diminution because the absorption data have not been corrected for (*1*) unknown apparent absorption due to the light-scattering of vitrain itself and of particles or (*2*) for the absorption of isolated benzene rings or non-aromatic substances or (*3*) for the absorption of free radicals.

Absorption indices at various wavelengths

The absorption indices, k, at various wavelengths, constitute the spectrum of this optical constant through the entire u.v.–visible region. ks and the corresponding Ks at several wavelengths in *Figure 1* are listed in *Table 6*;

$k = 2{\cdot}3\lambda A/4\pi xn$ and $K = A/bc$, where λ = wavelength of light in cm, A = absorbance or optical density, x = thickness of the coal sample in cm, c = concentration in g/l., b = cell thickness in cm, and n = refractive index. Values for n at various wavelengths were obtained from reflectivity spectra[12]. Compared with the absorption index obtained in the usual way, from reflectivity data at 5 461 Å, the present absorption data at 5 461 Å are considered more accurate[1]. The use of reflectance data and the Fresnel equation introduces large errors in the calculation of absorption indices because the Fresnel equation is nearly insensitive to these low indices.

Table 6. Specific extinction coefficients and calculated absorption indices using refractive indices determined from reflectivity spectra, Pittsburgh vitrain, 84 per cent carbon

Wavelength, Å	*Specific extinction coefficients, K*	*Absorption indices, k*	*Wavelength, Å*	*Specific extinction coefficients, K*	*Absorption indices, k*
7750	0·8	0·006	3500	14·5	0·066
7000	1·2	0·011	3000	20	0·079
6000	2·5	0·020	2750	23	0·088
5461	3·7	0·026	2500	24	0·086
5000	5·4	0·035	2200	28	0·093
4500	7·6	0·044	2100	29	0·093
4000	10·0	0·052			

CORRELATION OF FREE RADICALS AND COLOUR OF COAL

If the colour of coal is due to free radicals the absorption intensities in the visible region should increase quantitatively with the free radical content[1]. Ratios of the specific extinction coefficients at three wavelengths were compared previously with the ratio from Ingram's values for concentrations of free radicals in coals of 84 per cent carbon and 72 per cent carbon[1]. These data have been revised on the basis of recent electron paramagnetic resonance measurements. The new ratio of free radical contents correlates more closely with the ratios of absorption intensities (*Table 7*). This correlation indicates but does not prove that free radicals are an important cause of the colour of coal.

Table 7. Correlation of colour intensity and free radical content of lignite and high-volatile bituminous vitrains

Material	*Specific extinction coefficient of thin sections*			*Free radicals per gramme*
	7000 Å	5460 Å	4000 Å	
Pittsburgh vitrain (84 per cent carbon)	1·22	3·7	10·0	$0{\cdot}42 \times 10^{19}$
Velva lignite vitrain (72 per cent carbon)	1·25	2·6	6·1	$0{\cdot}15 \times 10^{19}$
Ratio	1·0	1·4	1·7	2·8

CONCLUSIONS

The various values calculated for maximum concentrations of polynuclear condensed aromatics are: (*1*) 11 per cent for van Krevelen's 23-component mixture, (*2*) 13 per cent for a hypothetical 47-component mixture of 5- and 6-ring compounds, and (*3*) 25 per cent based on total absorption areas for 14 compounds. These values are considered unrealistically high. In addition to scattering of light and absorption by other species, the lack of any fine structure in an absorbance plot of a vitrain spectrum constitutes evidence against the presence of 11 to 25 per cent of polynuclear condensed aromatics. For any complex mixture of such compounds there would be enough coincidences of intense bands to produce regions of high intensity and therefore spectral structure. High-temperature pitches definitely contain polynuclear condensed aromatics produced in the carbonization process, and their spectra show some fine structure. Vitrain, however, has no trace of fine structure.

The recent x-ray studies of P. B. HIRSCH indicate that the aromatic platelets in 84 per cent carbon coal are considerably smaller (1 to 4 rings)[13] than earlier measurements indicated[4]. The limitation to small aromatic nuclei means that (*1*) the variety of possible polynuclear aromatics is limited to naphthalene, phenanthrene, fluorene, pyrene, etc., and (*2*) the intense absorption bands for these small aromatic nuclei would be grouped together in the short wavelength region which therefore would show intense specific absorption. This does not occur.

If the principal structures in coal are not predominantly polynuclear aromatics then the important structures must be aliphatic and alicyclic and/or benzenoid. The shortage of hydrogen, oxygen and other elements requires that coal should contain an extensive system of tetrahedral C—C bonds including quaternary carbons in diamond-like structures of limited size.

The experimental work of H. Retcofsky and the provision of thin sections by the petrographic group of the Special Coal Research Section are gratefully acknowledged.

Branch of Coal-to-Oil Research,
Division of Solid Fuels Technology,
Bureau of Mines, Pittsburgh, Pa

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Recent Developments and Notes

VENEZUELAN COALS

AT the request of the Venezuelan government a detailed examination has been made of the coals from the Naricual coalfield, Estado Anzoategui, in the northern part of Venezuela, with the particular objective of investigating the possibility of their use in the iron and steel industry now undergoing considerable development in the country. A full account of the properties of these coals and of both laboratory and small scale industrial tests, has been published by E. F. DI GRAGNANO, of S.p.A. Vetrocoke, Turin [*Riv. Combust.* 1958, **12**, 847–885, 932–965].

These coals are of the tertiary era, with vitrinite as the chief component, though some have an appreciably high exinite content. They mostly give a high yield of volatile matter, 43 to 49 per cent d.a.f., and have a low agglomerating value, but the ash content is generally low, 4 or 5 per cent. The International Classification Code Numbers are 611, 621, 632, 633.

Considerable information is given as to the results of laboratory analyses and tests, including the Sheffield coking and Arnu dilatometer tests, the Roga caking power test, the Bauer–Koppers distillation test and the Koppers test for swelling power. Petrographic analyses were carried out and there is a considerable number of illustrations of microstructure of the coals and of the cokes obtained.

Several types of preliminary treatment of the coals prior to carbonization were examined, including hydrogenation, ultrasonic irradiation, adjustment of the composition of the coking charge on a petrographic basis, admixture of other materials to the coking charge and preliminary compression of the charge. The results showed that, both from technical and economic considerations, the best method is likely to be that of preliminary compression. A coking plant has now been designed on this basis for the production of coke to be used in the iron and steel plant which is being built for the Venezuelan government at Puerto Ordaz.

GAS AND FUEL CHEMISTRY IN THE AMERICAN CHEMICAL SOCIETY

In the last issue of *Bituminous Coal Research* [1958, **18**, No. 4, 15; BCR Inc., Pittsburgh] it is reported that R. A. GLENN, supervising chemist in BCR Inc., is Chairman for 1959 of the Division of Gas and Fuel Chemistry of the American Chemical Society. Dr Glenn, who has published many papers in the field of fuel technology, is a member of the National Research Council Committee on the Chemistry of Coal, National Academy of Sciences and a member of the Bituminous Coal Research Advisory Committee on Carbonization sponsored at the Pennsylvania State University by the Central Pennsylvania Coal Producers Association and the Western Pennsylvania Coal Operators Association.

DRAINAGE OF METHANE FROM COALFIELDS

In 1954 a number of experts visited the European coalfields under the aegis of the Organization for European Economic Cooperation [O.E.E.C.] to collect information as to the practice in different countries in the drainage of methane [*Drainage and Use of Methane from Coal-Fields* (*Firedamp*); January 1956; E.P.A. Project No. 163, O.E.E.C.]. In May 1958 these experts met again to consider the progress made since the issue of their original report. Western Germany, Belgium, France, the United Kingdom and the Saar were represented at the meeting and a document which is to be regarded as an addendum to the earlier report has now been published [*Drainage and Use of Methane from Coal-Fields: Developments since 1956*; December 1958; O.E.E.C.].

Considerable progress was noted in all the above countries in drainage and drilling methods and in the use of scientific control and safety devices. The use of methane has also been extended to more industries for power purposes, and also for use in town gas supply and for the manufacture of chemicals. Analysis of the conditions of degasification of coal seams has led to considerable progress in establishing the basic principles of firedamp emission. More extensive knowledge has been obtained of the factors influencing emission and of their interdependence. Emphasis is put upon the importance of the prior determination of possible firedamp output in specified conditions of work.

The largest contribution in the document from any one country is that regarding developments in Belgium, particularly with respect to drainage technique, which consists of drilling bore-holes from the headgate in the long-wall face, linking them to the collecting mains and applying suction through an exhauster at the pithead. Reference is specially made to the value of applying strong suction to the bore-hole and correspondingly reducing the total number of holes; the long tubing technique; drilling of a series of bore-holes in various directions; drilling of bore-holes in the floor.

In Great Britain most of the firedamp drained is obtained by the conventional cross-measure bore-hole method, although at one colliery all the drained gas is drawn from the worked-out areas and at another colliery some gas is obtained from the seam ahead of a long-wall face. Firedamp drained from mines in this country is used directly for boiler firing and as town gas, either by mixing it with coal gas or by reforming it. Up to the present such firedamp is being used by the Wales Gas Board at Point of Ayr and the Maelor gasworks, both in North Wales, and at the Aberavon gasworks, Port Talbot, South Wales; by the Northern Gas Board, at Whitehaven; by the West Midlands Gas Board at Stoke-on-Trent; and by the Scottish Gas Board at the gasworks at Provan, Glasgow, and at Dunfermline.

EUROPEAN ENERGY STATISTICS

The O.E.E.C. has recently published *Basic Statistics of Energy for O.E.E.C. Countries* [December 1958]. There is no attempt in this bulletin to draw up an energy balance sheet, but simply to provide the basic data from which the different types of balance sheet can be calculated rapidly. The material is

divided into two parts, Part I giving the statistics for each year from 1950 to 1957 inclusive for the energy situation in the area constituted by all métropolitan countries which are members of the O.E.E.C. This part is divided into two sections, one consisting of tables by sources of energy and the other consisting of eight tables each covering one year in the period 1950–57, grouping and condensing the data relating to all sources of energy for the year concerned. Part II contains tables by countries for the year 1957, similar to those supplied for the O.E.E.C. area as a whole in the second section of Part I.

'STRUCTURAL INDEX' OF COAL

In a paper by S. S. URAZOVSKII, V. A. VOLOSHIN and A. I. VYSOTSKAYA, relationship between the heat of combustion and structure of gas coal and of the solid products of carbonization is considered [*Dokl. Akad. Nauk S.S.S.R.* (*Rep. Acad. Sci. U.S.S.R.*) 1958, **120** (3), 595]. The relation put forward by J. SCHUYER and D. W. VAN KREVELEN [*Fuel, Lond.* 1954, **33**, 348] is criticized on the ground that they took account of structure within the molecule but not of intermolecular structure. From an equation of M. S. KHARASCH ['Heats of combustion of organic compounds.' *Bur. Stand. J. Res., Wash.* 1929. **2**, 359 to 430], an expression for a *structural index* is derived, representing the total effect of structure on the heat of combustion of a compound. The structural index is plotted against the temperature at which a coal is heated and is shown to rise to a peak value at 540°C, corresponding with the structure of coke formed at that temperature.

METHANE FROM CARBON

J. D. BLACKWOOD, Division of Industrial Chemistry, C.S.I.R.O., Melbourne, has made a further communication on his research in connection with the production of methane from carbon, in the form of coconut char, when it is allowed to react with steam under pressure [*Nature, Lond.* 1958, **182**, 1014; see also J. D. BLACKWOOD and F. MCGRORY, *Austral. J. Chem.* 1958, **11**, 16]. The rate of formation of methane is a linear function of the steam pressure and appeared to be independent of the partial pressure of hydrogen when the latter was small. A similar study of the reaction of hydrogen and carbon under pressure at 650° to 950°C has shown that the rate of formation of methane is a linear function of the hydrogen pressure and that the addition of small amounts of steam to the atmosphere of hydrogen has no apparent effect on the rate of formation of methane. It is suggested that the mechanism of methane formation is the same in both reactions.

It is suggested that the carbon–steam reaction is controlled by oxygen groups attached to the carbon and that the methane produced is formed by reaction of steam with adsorbed hydrogen, liberating methane and carbon monoxide. In the reaction of hydrogen with carbon it is believed that methane may be formed by the intervention of oxygen groups, such as chromene or benzpyran, in the carbon structure, and these may also be effective in the carbon–steam reaction.

CHEMICALS, OIL AND GAS FROM COAL: NEW INVESTIGATIONS

In the House of Commons on 16 April Sir IAN HOROBIN, Parliamentary

Secretary to the Minister of Power, replied to a question as to what further action the Government proposed to take to investigate possible methods of converting coal into chemicals, gas and oil. After referring to the research and development work of the Ministry of Power, along with other Government Departments and outside interests, which is being carried out on the problems of processing coals to produce chemicals, gas for fuel purposes, and various types of hydrocarbon oils, he stated that in view of the need to make the best use of our coal resources, the Minister of Power feels that the time has come when this work and any other possibilities which may offer prospects of expanding the use of coal for these purposes should be reviewed by an authoritative and independent body.

He has accordingly decided, after consultation with Sir ALEXANDER FLECK, Chairman of his Scientific Advisory Council, to set up a Committee with the following terms of reference:

> To review the work that has been done in recent years on the development of processes in which coal is the basic raw material and which will produce marketable products of a chemical or a gaseous or liquid hydrocarbon type; and to make recommendations as to the direction of further research and development work on any such processes which appear to the Committee to hold promise of industrial application and as to the type of organization or organizations best suited to carry out such work.

Mr A. H. WILSON, F.R.S., Deputy Chairman and Managing Director in charge of research and development for Courtaulds Ltd, is to be the Chairman of this Committee. The other members will be Mr M. A. L. BANKS; Mr HENRY BENSON, C.B.E.; Mr H. E. COLLINS, C.B.E.; Captain W. GREGSON, C.B.E.; Dr R. HOLROYD; Mr W. K. HUTCHISON, C.B.E.; Dr M. A. MATTHEWS and Mr B. E. A. VIGERS.

The Committee will be assisted in its work by two Assessors, Mr S. H. CLARKE, C.B.E., Director of the Warren Spring Laboratory of the Department of Scientific and Industrial Research, and Mr D. A. B. LLEWELLYN, Ministry of Power. The Secretary of the Committee will be Mr W. R. G. BELL of the Ministry of Power, to whom all communications regarding the work of the Committee should be addressed.

The Report of the Committee will be presented to Parliament.

SALTERS' INSTITUTE OF INDUSTRIAL CHEMISTRY

Professor A. R. J. P. UBBELOHDE, F.R.S., Professor of Thermodynamics at the Imperial College of Science and Technology, London, has been appointed Director of the Salters' Institute of Industrial Chemistry on the retirement of Sir ALFRED EGERTON, F.R.S., on 30 June 1959.

INTERNATIONAL CLEAN AIR CONFERENCE

The Conference organized by the National Society for Clean Air to celebrate its Diamond Jubilee will be held in the Seymour Hall, London, from 20 to 23 October. Already nearly 50 oversea delegates, representing 15 countries, have been appointed. Papers are invited and all accepted contributions will be printed and distributed in advance of the Conference and will be discussed rather than read. Proposals for contributions should be made to the Director,

National Society for Clean Air, Palace Chambers, Bridge Street, London, S.W.1, from whom further details about the Conference are available.

BENZOLE TECHNOLOGY

The *Review of Benzole Technology 1957* has recently been issued by the National Benzole and Allied Products Association (132–135 Sloane Street, London, S.W.1; 21*s* or 22*s* 6*d* post free). This is the fifth annual volume of the *Review* and the information covers production from carbonization processes, benzole recovery, production of aromatic hydrocarbons from other sources, benzole refining, properties, industrial uses of benzole, motor fuels and internal combustion engines, analytical methods, safety and handling, economics and statistics. There are over 1200 bibliographical references.

The total production of crude and refined benzole (in gal $\times 10^6$) in 1956 and 1957 was as follows:

		1956	1957
Crude benzole:	coke ovens	84·7	89·2
	gasworks	27·7	25·8
	tar distilleries	7·9	7·4
	Total	120·3	122·4
Motor benzole:		52·0	48·3
Pure benzole, all grades:		25·4	32·3

The considerable increase in the production of pure benzole is accounted for partly by the increase in crude benzole production at coke ovens and partly by refining to pure grades instead of to motor benzole. In the past 20 years there has been a very considerable trend away from motor benzole produced from coke ovens. This is shown by data of W. GREEN in his presidential address to the Coke Oven Managers' Association in 1958 [*Coke Oven Managers' Year Book*, 1958, 17].

	Crude benzole produced at coke ovens, gal $\times 10^6$	Used in motor fuel, gal $\times 10^6$
1938	57·3	31·6
1946	60·1	32·5
1956	84·7	25·6

CHINESE SCIENTIFIC LITERATURE

The Lending Library Unit of the D.S.I.R. has started to collect Chinese scientific literature. About 150 Chinese periodicals are now on regular order and the first batch has arrived at the Library's London premises.

This is announced in the March issue of the recently introduced *L.L.U. Translations Bulletin* [published for the D.S.I.R. by H.M.S.O., price 4*s* (4*s* 5*d* by post)]. In a special article, the *Bulletin* suggests that the scientific output of China, which may be growing rapidly, cannot be ignored. The contents of the Chinese publications being received are to be assessed, and a scientist with a knowledge of Chinese is being recruited by L.L.U. to select and promote the use of Chinese scientific and technological literature.

NEW UDEX UNIT IN OIL REFINERY

A new plant, known as the Udex unit, is now in operation at the Stanlow refinery of the Shell Petroleum Company Ltd at Ellesmere Port, near Chester,

for the production of an important blending component for aviation gasoline. It is the first of its kind in any Shell refinery.

Construction of the Udex unit, which cost about £800 000, began at the end of 1957 and its acceptance trial has recently been completed. The unit incorporates six columns, the tallest of which is a 120 ft solvent stripper, and the capacity of the unit is 1000 tons per day. It was designed by the Universal Oil Products Company of Des Plaines, Illinois, U.S.A.

The Udex unit is of the solvent extraction type using a solvent mixture of diethylene glycol, dipropylene glycol and water. The feedstock is a product of the Stanlow Platformer. In this process the solvent mixture flows down the column and is dispersed in the rising hydrocarbon stream by the use of inverted bubble-cap plates of special design. Diethylene glycol is not sufficiently selective to produce pure aromatics from a mixed hydrocarbon feed. Addition of water increases the selectivity, so that aromatics are dissolved and paraffins rejected, though the solubility is reduced. By adjusting the temperature and the water content, and by refluxing both raffinate and extract, benzene of 99·9 mol per cent can be obtained [see F. MORTON, *J. Inst. Chem.* 1959, **83**, 146]. The aromatic extract is used in aviation gasoline, whilst the insoluble raffinate will be used as an additional feedstock for other processes. Operating on a platformate containing C_6, C_7 and C_8 hydrocarbons, the Udex process will give extracts containing up to 98 mol per cent of aromatic hydrocarbons.

NEW DISTILLATION UNIT AT SHELL HAVEN

A second crude oil distillation unit is now on stream at Shell Haven refinery in Essex on the Thames estuary. The cost of the unit, with tankage and ancillary equipment, is approximately £6½ million, and its daily capacity is 11000 tons of Middle East crude oil. Its operation approximately doubles Shell Haven's distilling capacity to about 8 million tons per annum. With the addition of Stanlow, Heysham and Ardrossan refineries, Shell's total refinery capacity in the United Kingdom is now increased to some 15 million tons per annum.

The new distillation unit, designed by Shell technologists in Holland, has two special features. First, a high degree of heat recovery is employed so that fuel consumption in the operation of the unit will be some 30 per cent lower than in previous designs. Secondly, a good recovery of light hydrocarbons is obtained by the use of a large high speed centrifugal compressor which receives all the uncondensed streams and delivers them to the gas fractionating columns.

TRANSPORT OF LIQUID METHANE

On 20 February the tanker *Methane Pioneer* arrived at Canvey Island, Essex, with the first load of liquefied natural gas ever to be carried by sea, marking the successful completion of the first stage in an experiment which may have important consequences. It will be necessary for three or four more trial voyages of this nature to be undertaken before the technical and economic possibilities of the project can be fully assessed.

Methane Pioneer, a dry cargo boat converted for this purpose at a cost of about £1·6 million, left the Gulf of Mexico on 31 January. The ship is owned and operated by British Methane Ltd. This is a company formed by the Gas Council of Great Britain and Constock International Methane Limited, an American company which has carried out research and development work in this project for a number of years. The experimental load consisted of 2000 tons of liquefied natural gas from one of the Gulf Coast oilfields. After liquefaction at − 258°F, which reduces its volume by 1/600, it was loaded into five special tanks in *Methane Pioneer*. The tanks are of aluminium with a 12 in. insulation of balsa wood and an outer jacket of steel. During the voyage of 23 days from Lake Charles, La, evaporation loss was less than 10 per cent, somewhat lower than predicted. A tanker is now being designed in which the methane lost by evaporation may be recovered and used to supplement its fuel supply.

The liquid was pumped from the tanker through a pipeline with a 6 in. covering of insulation to two tanks specially designed to receive the liquid. Each of the storage tanks has a capacity of about 1000 tons of the liquid. Although the shore storage tanks are heavily insulated there is a continuous boil-off of gaseous methane from the liquid, and this material is contained in a small gas-holder of the dry-sealed Wiggins type, whence it is pumped into the mains system. Liquid methane is then converted by heat exchange with water or steam into gas under pressure, and this pressure of up to 270 lb/in^2 will be used to convey the gaseous methane into the North Thames Gas Board's transmission lines where it will mix with refinery gases from the Shell Haven refinery.

The town gas supplied by the N.T.G.B. is distributed at 500 B.Th.U./ft^3, while methane has a calorific value of 1000 B.Th.U./ft^3, and reforming of the methane into gas of 500 B.Th.U./ft^3 will be carried out at Romford by the Onia–Gegi catalytic process in a plant built for the Board in 1958 by Humphreys and Glasgow Ltd, for treating refinery tail gas from Shell Haven. The gas after reforming will have similar characteristics to gas normally produced from coal and will be suitable in every way for consumers' appliances, with the added advantage that it will be free from sulphur.

Natural gas in its original state has an equivalent of approximately 530 therms per ton. Allowing for losses during the conversion processes and during the voyage it is estimated that the net value to the gas industry will be approximately 480 therms per ton. This means that the equivalent capacity of the trial shipment of 2000 tons will be a little short of one million therms. If the trials prove successful, both from the technical and economic points of view, consideration will be given to the import of liquid methane on a much larger scale. Vessels carrying some 30000 tons will probably be required in order to secure real economy. The costs of the experimental shipment are being shared by the British gas industry and the American interests concerned.

Work is now beginning on a similar project in France. Liquid methane would come from the Hassi R'Mel field in the Sahara and development is being carried out by Société d'Etude du Transport et de la Valorisation des

Gaz Naturels du Sahara, a combine formed by Air Liquide and four oil companies operating in the Sahara.

The developments during the past 20 years to provide suitable static containers for liquid methane and receptacles for use in its transportation by water-borne craft were reviewed in a lecture by C. I. KELLY, given to the Economics and Operations Group of the Institute of Petroleum last November [*Inst. Petrol. Rev.* 1959, **13**, 106].

FUEL INFORMATION FOR ARCHITECTS

A series of supplements, sponsored by the Gas Council, has been appearing in the *Architects' Journal*, with the object of giving architects full technical information about the uses of gas and coke. The series, when complete, will comprise an *Architects' Handbook*, and reprints will be available in bound form. A limited quantity of the reprints can be obtained on application to the Area Gas Boards or The Gas Council, 1 Grosvenor Place, London, S.W.1.

ADIABATIC BOMB CALORIMETER

Of the three possible types of jackets for use in bomb-calorimeter systems, usually referred to as static, isothermal and adiabatic, it is the last of these which is particularly suitable where many determinations of calorific value are required each day. The best known adiabatic calorimeter is that devised by the American fuel technologist S. W. PARR, as long ago as 1912. The first of this type to be manufactured commercially in the United Kingdom is the Gallenkamp Automatic Adiabatic Bomb Calorimeter which has recently become available.

It has been designed for the maximum number of determinations daily at very high accuracy. The unique design of the water jacket and control system enables the jacket to follow the temperature of the calorimeter vessel with considerable precision at all stages of each test. Corrections for heat exchange between the calorimeter and its surroundings are thus eliminated.

The calorimeter is entirely enclosed in a water jacket, instantaneous heaters in which, controlled by a very sensitive system, restore equilibrium when the temperature of the jacket falls below that of the calorimeter vessel. Temperature differences are detected by two thermistors which form opposite arms of a Wheatstone bridge, the amplified output from which actuates the heaters.

After the bomb is charged and placed inside the calorimeter, it is only necessary to switch on the equipment for a few minutes and the water jacket temperature, previously adjusted to be below that of the calorimeter by means of a built-in cooling coil, automatically equalizes with that of the calorimeter. The initial temperature is then recorded and the bomb fired from a built-in transformer. As the calorimeter temperature rises, the water jacket temperature follows to within 0·25°C during the chief period of increase. It is possible to do a complete determination in about 20 minutes, including the calculations.

The following experimental results show the precision with which the calorimeter operates. During one typical run, over a pre-firing period of

seven minutes the temperature of the calorimeter varied between 27·406° and 27·405°C. The bomb was then fired and in six minutes the calorimeter reached a temperature of 28·837°C which increased to 28·839°C after two minutes, and remained at that value for a further six minutes. The adiabatic bomb has been on field trial at a power station within the S.E. area and its use has resulted in a reduction by 60 per cent of the time taken for calorific value determinations by other methods.

AMERICAN RESEARCH ON COAL-BURNING GAS TURBINE

Since 1945 the Locomotive Development Committee of Bituminous Coal Research Inc. has carried out research and development work on the coal-burning gas turbine. During this time about 5½ million dollars have been spent by the coal companies and railroads sponsoring this programme. It is now announced that the equipment used in this work, and the technical knowledge arising therefrom, are to be made available to the U.S. Bureau of Mines which is to expand the research to establish the feasibility of the coal-burning gas turbine for power generation in stationary plants [*Bituminous Coal Research*, 1959, **19**, No. 1, 3]. The gas turbine installation of 4200 h.p., valued at 1·2 million dollars, is the main item of the equipment being lent to the Bureau of Mines.

The original objectives of the research undertaken by BCR to develop the coal-burning gas turbine for motive power use have been achieved. The three basic problems involved were: (*i*) feeding coal to the chamber at elevated pressures, (*ii*) burning coal at high temperatures and pressures, (*iii*) ash control and elimination. Coal combustion has been accomplished at an efficiency of 97 per cent in a film-cooled jet aircraft-type combustion chamber of special design. In regard to ash control, dust collection efficiencies exceeding 92 per cent have been achieved, but the Bureau of Mines will seek even better fly ash control. The coal feeding problem was solved by a special design of coal pump that provided metering and pressurized feeding of the pulverized coal.

FUELLING JET AIRLINERS

Part of the aviation research now being conducted at Thornton Research Centre, the major laboratory of the Shell International Petroleum Company Ltd in the United Kingdom, is directed towards developing airfield fuelling equipment to meet the changing demands of new types of airliners. Much of the work is common both to fuelling by mobile vehicles and by hydrants, although the latter introduce their own special engineering problems.

There are many new and difficult problems connected with the rapid, economic and safe fuelling of the huge jet aircraft now being used. Modern jet airliners, such as the Boeing 707 and the Douglas DC–8, which consume up to 2000 gallons of fuel an hour, may require fuel uplifts of some 16000 gallons. These large quantities of fuel need to be delivered, using underwing pressure fuelling, at the rate of 1000 gallons per minute, in order to keep ground time to a minimum. These requirements will be met by using either large mobile fuelling vehicles of up to 10000 gallons capacity, or by hydrant systems capable of pumping at the rate of 4000 gallons per minute when servicing four aircraft simultaneously at large, busy airports.

The quality control system devised by Shell ensures that clean and water-free fuel is supplied to aircraft. This includes a number of techniques and different pieces of equipment, one of which is a microfilter. Work is now in progress on methods for reducing to a minimum the amount of solids in the fuel, including particles as small as one or two microns. At Thornton, methods of evaluating filters have been developed and for the evaluation of microscopic material counting is performed by the Casella electronic particle counter-and-sizer machine.

In connection with the problem of ice formed on very fine engine filters by minute amounts of water contained in the fuel, modern turbine-engined aircraft are equipped with fuel heaters, or similar devices, to combat this hazard. However, the amount of water contamination with which such equipment can cope is limited. The small amount of water that may be dissolved in the fuel cannot be removed by filtration or other mechanical means. The fuel supplied to the aircraft on the ground can only be free of water to the extent of removing all undissolved water and this is the aim of the work which has been carried out at Thornton.

In respect of undissolved water, the kerosine type of aviation turbine fuel presents a greater problem than more volatile fuels by reason of its higher viscosity and rather high gravity which causes the water to be held in dispersion very much longer. For the elimination of dispersed or free water from fuels, settling in tanks has proved effective, but alternative methods, for example, water separators, are becoming available and one of the studies is to determine how effective they would be in service.

To check that water is not present in the fuel at the time of fuelling, a detector has been introduced and constitutes an essential part of the control system. Its use allows an operator to determine positively whether free water is present in the fuel. Under development is the Fuel Monitor, a valve system for installation on the fuelling vehicle, which automatically closes when water is present in the fuel flowing through it [see *Fuel, Lond.* 1959, **38**, 90].

In fuelling operations no trouble with static electricity has so far been experienced, mainly because the flow rates have been relatively low and/or because there has been adequate time for relaxation of charges in the hoses following the equipment in which most of the charge has been developed. For future operations these factors may be subject to change and are included in a general study of the problem of static electricity. One method of dealing with the problem is to increase the conductivity of the fuel handled to such an extent that the charges developed flow away rapidly to the earthed containers. The conductivity levels of fuels in practice tend to be rather low, but they can be raised by means of suitable additives. This approach is being worked on by Shell and various additives are under current development.

The advantage of the hydrant method of fuelling is that large quantities of fuel can be delivered to a number of aircraft simultaneously with the minimum congestion of equipment on the apron. Hydrant fuelling has been in use for a considerable number of years but continuous development and research are necessary to meet the demands for high fuel flow rates and quantities.

One of the problems under special investigation is the development or hydraulic shock in a pumping system when valve closure occurs. This problem is one which arises during the fuelling of aircraft as a result either of the closure of the aircraft tank valves or of the closure of valves in fuelling equipment. The primary problem is to isolate the aircraft system from any shocks which occur and the secondary problem is to protect the ground equipment. Special valve control gear may be used to isolate the aircraft system from high upstream surges, or pneumatic devices to increase the elasticity of the fluid in the system and thereby reduce the magnitude of the shock created.

B.C.U.R.A., 1938–1959

In April 1938, the British Coal Utilisation Research Association was formed to 'promote research and other scientific work in connection with the utilization of coal and its derivatives'. To mark the 21st anniversary there were open days at its laboratories in Leatherhead from 22 to 24 April, the first day being for members of the Association and special guests, the second for representatives of Government Departments, Research Associations, Universities and Technical Colleges, and the third for students from local colleges and schools. On the first day the guest of honour was the Rt Hon. Lord Mills, K.B.E., Minister of Power.

The B.C.U.R.A. is now one of the largest of the 39 industrial research associations sponsored by the Department of Scientific and Industrial Research. Its growth is illustrated by the increase in its annual income, which has risen from £28000 in 1938 to £70000 in 1942, £201500 in 1947, and £413000 in 1958. Of its total staff of some 300, 80 are graduates, who are representative of most of the recognized fields of physical science, from mathematics through the several branches of chemistry and physics to engineering, and there is a similar number of research assistants.

The Association is supported by the National Coal Board, the Electricity Council, the Gas Council and the British Transport Commission, and about 150 other members, both individual firms and trade associations.

Research at Leatherhead is being directed especially towards (*a*) improving and devising appliances suitable for burning small coal, (*b*) developing methods for the automatic control of combustion, (*c*) devising means for measuring and reducing atmospheric pollution from coal-burning appliances, and also (*d*) the development of new products from coal.

One of the most important of current needs is a method for converting small coal cheaply to gas, and ultimately to oil. The Association's experimental slagging gasifier, built under contract with the Ministry of Power, at present consumes about a ton of fuel an hour and can take, in short tests, up to half of this in the form of pulverized coal. It has been operated successfully at various ash levels and over a range of ash fluidities.

The small-pipe, forced-circulation central heating system developed by the Association offers many advantages over conventional central heating systems, and represents a major contribution of research towards better use of solid fuel in the home.

Following the development by the B.C.U.R.A. of the free-standing convector fire with restricted throat, over 30 designs of this type of appliance are now on the market, and more manufacturers are planning production.

A method of automatic control for a miniature chain-grate stoker, used to fire central heating boilers (½ to 2 million B.Th.U./h) in offices or blocks of flats, has been devised, and this permits ½ in. small coal to be burnt smokelessly at high efficiency over a wide range of heating loads.

New, and more accurate, methods of measuring domestic smoke emission have been developed at Leatherhead. A first step towards the reduction of pollution from coal-burning appliances has been made through work on the measurement of dust and grit emission from boiler furnaces, which has aroused much interest from those concerned with enforcing or complying with the Clean Air Act.

To mark the 21st anniversary of the Association and to survey its work up to date, a *Bibliography of Publications 1938–1959* is to be issued in the near future. The bibliography is intended to serve the practical purpose of making it easy to locate accounts of the Association's researches. It has the further interest of epitomizing the history of 21 years of coal research.

ANTHRACOLOGIC ANALYSIS

A monograph providing a general review of the nature and uses of coal petrology and its application particularly to Ohio coals has recently been published by G. H. CADY, of the Division of Geological Survey, Ohio [*Inform. Circ. Ohio geol. Surv. No. 22*, 1958, 83 pp]. The author has made many contributions to knowledge in this field during the past 25 years and is a member of the International Committee of Coal Petrology. It has become generally recognized in recent years that, in addition to knowledge of the chemically distinguishable constituents of coal as revealed, for example, by rational analysis, it is essential to have information of the physically distinguishable components of coal in order to make discriminating selection and carry out suitable preparation of coal for specific uses. Greater importance is now being attached to the relation between the physical heterogeneity of coal as a mass of coalified plant structures and the variations that accompany differences in screen size. The primary objective of petrological analysis of coal material is its classification in terms of palaeobotanical entities of distinctly different genesis or physical attributes. There arises in this way a classification of coal of fundamental importance irrespective of rank.

The introductory section of the monograph is written with the aim of presenting a picture of this comparatively young science, referred to as anthracologic analysis, to assist in reducing the present lack of uniformity in terminology and methods which prevents the attainment of a common understanding of the physical structure and composition of coal. The International Committee of Coal Petrology is endeavouring to establish a standard international system and terminology of coal petrology, with the [European] Continental system of coal petrology as a basis, but with recognition of the system of coal microscopy largely peculiar to the United States of America. The fundamental differences between these two systems of coal description and analysis are explained and discussed in the monograph.

Other sections deal with the techniques of graphic coal bed profiles or descriptions, on the basis of both megascopic and microscopic criteria; procedures for analysis of broken coal produced by mining and preparation processes, or by the deliberate crushing of column samples; and the application of profile and broken coal analyses in geological and practical fields.

PUMPING OIL AND WATER

The joint pumping of petroleum and a small quantity of water along pipelines removes the necessity for heating stations at intervals when the oil alone is pumped over long distances [see *Fuel, Lond.* 1959, **38**, 219]. These pipelines have a helical rifling on the inner surface, or the rifling may be replaced by a wire placed in spiral fashion inside the pipe. The presence of the rifling or wire causes an aqueous film to be formed on the internal surface of the pipe which sharply decreases the hydraulic resistance when petroleum and water are pumped.

The hydraulic theory of this effect has been examined by V. I. CHEMIKIN [*Trudi mosk. neft. in-ta No. 17*, 1956, 101; *Referat. Zh. Mekh., No. 4*, 1957, Rev. 4245]. In particular he examines the case when, in accordance with observations, turbulent conditions occur in the annular flow of water, whilst the flow of petroleum takes place in laminar conditions. The conditions of stability of the aqueous film are also considered and relationships are derived for determining its thickness at given rates of flow of water and oil [V. A. ARKHANGEL'SKII, courtesy *Referativnyi Zhurnal*, U.S.S.R. translation, courtesy Ministry of Supply; *Appl. Mech. Rev.* 1959, **12**, 113].

MELCHETT MEDAL FOR 1959

The Melchett Medal of the Institute of Fuel for 1959 is to be awarded to Dr P. O. ROSIN. The medal will be presented to Dr Rosin at the Annual Dinner of the Institute at Grosvenor House, London, on Tuesday 13 October, and the Melchett Lecture will be delivered before the end of this year.

Dr Rosin was born in 1890 at Freiberg. He studied science, mining and metallurgy and obtained his Dipl. Ing. at Freiberg in 1914. He served in World War I from 1914 to 1918. After the war he obtained the degree of Dr. Ing. at Dresden in 1920. He was lecturer in metallurgy at the Mining Academy, Freiberg from 1920 to 1932, and became a Professor in 1927. He was a Professor at the Technische Hochschule, Charlottenburg, in 1932, and a research worker at the Imperial College, University of London, from 1936 to 1945; in World War II he became a British subject and was leader of a research team at the Imperial College for the Petroleum Warfare Department which worked on flame throwers and FIDO. He received a royal award for inventors. Since then he has continued his practice as an industrial consultant.

Dr Rosin's publications have been chiefly concerned with different aspects of fuel efficiency, particularly the preparation, use and economics of pulverized fuel, specially brown coal; principles of drying, grinding and sifting; size distribution law (with Rammler); thermodynamics and aerodynamics of combustion; *It* diagram of combustion (with Fehling); dynamic similarity

and use of models; low-temperature carbonization and gasification. Dr Rosin was elected a Fellow of the Institute of Fuel in 1938 and has served for many years as a member of Council, being Chairman of the Publications Committee from 1945 to 1951.

ATHABASCA TAR SANDS

Plans are being made to apply a nuclear explosion to produce oil from the Athabasca tar sands in Alberta [*Chem. Engng*, 1959, **66**, No. 4, 62]. It is proposed to detonate a small nuclear device at a depth of 1200 to 1400 ft underneath a 200 ft bed of tar sands. It is anticipated that a twofold effect will be produced; first, the blast pressure will break up the sand, making it more permeable, and secondly, the heat from the blast will convert the solid bitumen to a liquid fluid enough to be pumped from the ground through the drill pipe. Negotiations are now taking place to secure permission from the Canadian government to use a nuclear device. Various schemes advanced up to the present time to exploit the vast potential oil reserves of these sands are limited to that 2 per cent of the total deposits which can be mined by current methods.

RUSSIAN PATENTS

A *Russian Patents Gazette* is being published semi-monthly from January onwards by the Technical Information Company, Chancery House, Chancery Lane, London, W.C.2. The first issue, for January, was announced to be available in June and subsequent issues will be published rapidly to bring the *Gazette* up to date. Its editors are Dr M. M. BARASH and Dr P. L. B. OXLEY. The *Gazette* will contain abstracts in English of all new Russian patents and invention certificates, arranged under 91 class headings. The subscription rates are: (*i*) Russian Patents Gazette (Comprehensive), £32; (*ii*) General, Mechanical and Electrical Section only, £20; (*iii*) Chemistry and Chemical Engineering Section only, £20.

W. A. KIRKBY

COMBUSTION AND FLAME

Readers of *Fuel* may like to know that *Notes* appeared in the June issue of *Combustion and Flame* dealing with:

Fuel consumption tester
Flue gas corrosion
Fire protection

Publications

GLASS-MELTING TANK FURNACES

R. GUNTHER: translated from the German by J. CURRIE. Sheffield: Society of Glass Technology, 1958. *xiv* + 232 *pp.* (illus.) 60*s* or $9.00

THE glass-melting tank furnace introduced essentially in its present form by FREDERICK SIEMENS about 1870 is thermodynamically good in so far as it is continuous and not batch and uses a fair proportion of the waste heat of the combustion gases below the fusion temperature to preheat the combustion air. Attempts have been made to improve it further by introducing a counterflow heating process either with a column of batch briquettes in a shaft or with freely falling batch powder, but these have not found success and are not mentioned in this book, although there is a historical chapter by G. STEIN describing the early evolution of the tank furnace. The problem that confronts the designer of a furnace to melt and maintain a charge at a high temperature for a long time is well illustrated by the Sankey diagram of a glass tank heat balance on page 176. The wall heat losses from the furnace are more than three times the useful heat given to the batch while the wall losses from the regenerators and ports are a further one and a half times the useful heat and the final stack losses a further one times the useful heat. However, the great value of this book is that it covers systematically all the more scientific aspects of the design and use of this particular type of furnace which is the source of nearly all our glass. The treatment of most aspects of the fuel technology of such furnaces is clear and accurate although the reviewer feels that the work of the International Flame Research Committee might have been used to supplement the statement (page 158) that 'numerical calculation of luminous radiation has not yet been sufficiently developed for application to furnace practice'. Luminous radiation has always been of great importance as a mechanism of heat transfer in glass tanks and with the increased use of oil firing it is assuming even greater importance and it is essential to make some allowance for it if any reasonable prediction of heat transfer is to be made. Recent attempts to calculate the efficiency and output from first principles by a heat balance in stages along the flame are not mentioned and the use of models for gas flow and glass flow does not receive quite the importance that one might expect. These are, however, only criticisms of emphasis, and the book is certainly an essential for anyone concerned with the design, fuel economy or operation of glass tanks.

M. W. THRING

GAS CHROMATOGRAPHY, 1958

Edited by D. H. DESTY. London: Butterworths Scientific Publications; New York: Academic Press; 1958. *xiii* + 383 *pp.* (illus.) 70*s* or $12.00

THE subject of gas chromatography has aroused such widespread interest in the last few years that a number of symposia have been arranged on the subject. In May 1958 the Gas Chromatography Discussion Group held such a meeting in Amsterdam under the joint auspices of the Hydrocarbon Research Group of the Institute of Petroleum and the Koninklijke Nederlandse Chemische Vereniging. This book contains the complete proceedings of the Conference including not only the papers presented, but also the introductory lectures given by the section chairmen and the discussion that took place after each paper.

The subjects dealt with fall under four main headings: (*1*) theoretical treatments of the chromatogram; (*2*) determination of the role of the support and the stationary phase; (*3*) instrumentation; and (*4*) applications.

The theoretical treatments differ from earlier papers in that experimental verification of the parameters involved in the equations was sought for. The most notable papers in this group were those by GOLAY and GLUECKAUF. GOLAY gave a detailed treatment of the coated capillary column together with some results attained with this type of chromatogram.

GLUECKAUF described the separation of highly radioactive gases taking advantage of the heat output of such gases to improve desorption. Like GOLAY's paper, this is an elegant combination of theory and practice.

SCOTT and also BOHEMEN and PURNELL described the construction, use and theory of long packed columns giving efficiencies of up to 30000 theoretical plates. Such high efficiencies are also attainable with the capillary columns introduced by GOLAY and experimented with by DIJKSTRA and DE GOEY.

DESTY and his co-workers described detailed comparisons of the two common supports for the stationary phase, ground firebrick and Celite 545 and KWANTES and RIJNDERS dealt with the determination of activity coefficients from chromatographic data alone.

Under instrumentation there are two papers on katharometers, one by STUVE describing the use of filaments from small low voltage electric light bulbs. Two new detectors are introduced, one of very high sensitivity (the flame ionization detector developed by MCWILLIAM) and one of lower sensitivity but useful specificity (the flame emissivity detector developed by GRANT). Other papers dealt with programmed column heating, fully automatic sampling and large scale columns.

Applications of the technique dealt with halogen and interhalogen compounds, essential oils, volatile derivatives of amino acids, high boiling petroleum fractions and also phenols. The last paper in this volume deals with recommendations on the presentation of gas–liquid chromatographic data.

The discussion included after the formal papers adds useful material as well as clarifying obscure points. An author and subject index of these discussions is included. The editing is of the usual high standard expected from Mr DESTY and his collaborators and the publishers have done their part in excellent printing and arrangement. *In toto* this book represents a most useful addition to previous papers and books on the subject of gas chromatography.

A. T. JAMES

SECOND SYMPOSIUM ON COAL PREPARATION

Department of Mining, University of Leeds, 1959. Distributed by the Coal Preparation Plant Association, Sheffield. *xii* + 513 *pp*. 20*s*

IN 1952, the Coal Preparation Plant Association organized a Symposium on Coal Preparation at the University of Leeds. This was so successful that a Second Symposium was held in October 1957. The papers and discussions at the Second Symposium have now been collected in book form and published by the Department of Mining of the University of Leeds.

The publication is a very valuable contribution to coal preparation literature. It is not, of course, a textbook; it is confined to the subjects of the papers presented. Nevertheless, 67 people, including authors, took part in the discussions, and this in itself indicates the wide interest in the subjects selected, and ensures that for each of them a wide range of viewpoint was expressed. Indeed, the discussion of some contributions occupies as much space as the paper.

Of the 18 papers, five were contributed from the Mining Department of the University of Leeds, and four papers were from abroad; all were by acknowledged authorities on their subjects. Dr G. A. HERMANN MEYER presented a paper on hard coal briquetting plants in the Ruhr Coalfield, Dr P. J. MEERMAN described coal preparation research at the Dutch State Mines on the effect of interface-active chemicals, Dr P. J. VAN DER VAALT gave a most interesting paper on the problems of finding dense-medium materials in South Africa, and Dr D. A. DAHLSTROM gave a comprehensive paper on American experience in dealing with certain aspects of water clarification in washery circuits. In addition, Dr A. JOWETT, now on the staff of University of Leeds, presented an interesting paper on coal preparation in Australia.

Three papers dealt with dewatering, and four with froth flotation. Methods of expressing performance of washery plants and the value of comprehensive tests were covered in three papers; the future of coal preparation generally was well dealt with in a paper by G. H. ARROWSMITH. The papers by G. C. HARRIS and H. G. SMITH on moisture retention by fine

coal are two of the best papers on this subject to be found anywhere in the literature. Another excellent paper is that by S. AYTON and S. R. LOWE on traffic control at coal preparation plant sidings, a subject that has not received much attention in the literature; the paper treats it comprehensively.

The whole publication, amounting to over 500 pages, is of the highest quality. The Symposium was large enough to contain most of the recent significant advances in coal preparation, yet not so large as to inhibit extemporized discussion; the Proceedings range over a wide number of subjects and express modern views held by leading authorities, not only in Great Britain but in other parts of the world, on a variety of coal preparation problems. They form an excellent addition to the literature and should serve as a valuable reference book, both for the coal preparation engineer and the research worker.

W. R. CHAPMAN

THE CHEMICAL PROCESSING OF NUCLEAR FUELS

F. S. MARTIN and G. L. MILES. London: Butterworths Scientific Publications; New York: Academic Press, 1958. $x + 242$ *pp.* 40*s* or $7.50

THIS book, the authors state, is primarily intended for science and engineering students who have some acquaintance with nuclear reactor developments and are interested in the role of nuclear processing in nuclear power systems. The book is divided into five parts.

In *Part 1* the emphasis is on economics, it deals with the various types of reactors and fuel cycles of interest in a nuclear power industry, the formation and significance of fission products and heavy nuclides, and the general requirements of nuclear fuel processing. Much useful data are included but the treatment is somewhat advanced for the class of reader mentioned. Thus whilst it is true (page 10) that '^{239}Pu has the most satisfactory nuclear properties for a fast reactor fuel, . . .' this can only be deduced after manipulation of the values given for η and α in Table 1.1, and is not immediately obvious from it. Again the economic significance of fuel processing losses (page 54) can be derived from Table 5.2 but requires experience in the manipulation of the general equations.

Part 2 deals with aqueous processing methods and includes a useful summary of the solution chemistry of those elements of particular interest as fuels, fertile or canning materials or fission products. This leads on to the use of solvent extraction methods for the processing of nuclear fuels. Since these are the only methods currently in production use throughout the world the space allocated to the subject, and in particular to its technical aspects (27 of the total of 242 pages) is unduly small even in a work which sets out to emphasize 'the basic principles of fuel processing rather than the technology'. It is the more surprising therefore that in Chapter 9 the only method for the purification of plutonium for which space is allotted is the TTA process which, though of great interest, is now no longer used on a production scale. In the same chapter it is stated (page 102) that in the primary separation of uranium and plutonium using tributyl phosphate, an oxidation–reduction cycle is not used. This is not correct as is indicated in Figure 9.7 which shows ferrous sulphamate as the reducing agent.

Part 3 consists of a survey of the non-aqueous processes which have been studied for fuel treatment. Within the limitations imposed by the size of the book this survey is very well done though one feels that a more critical assessment of the methods described is desirable for the type of reader envisaged. This is met in part in paragraph 19.4 (Part 5).

Part 4 deals with effluent disposal and covers the ground adequately in terms of present and projected methods which, in this case, are critically reviewed.

Part 5 is a useful attempt to forecast future trends of development and serves to focus attention on to those aspects of the overall problem which, if improved, can lead to worthwhile economies.

The book is well produced and refreshingly free from misprints (Table 17.6 is incorrectly ascribed to Dunstan instead of Dunster). One minor source of irritation concerns the lists of references. These are inserted at the end of each of the five main parts of the book. In the absence of reference numbers at the head of each page, one is only able to locate the lists by consulting the Table of Contents to establish where, in fact, each part ends.

K. SADDINGTON

NOMENCLATURE OF INORGANIC CHEMISTRY 1957

International Union of Pure and Applied Chemistry: Butterworths Scientific Publications; London, 1959. *ix* + 93 *pp.* 15*s*

THIS work is a French and English issue of the rules drawn up by the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry: it is the outcome of many discussions on the 1953 *Tentative Rules for Inorganic Chemical Nomenclature*. The aim of the Commission has been to provide a logical system of nomenclature based on the composition and most obvious properties of substances, avoiding as far as possible theoretical matters liable to change. The rules are divided into the following sections: Elements; Formulae and Names of Compounds in General; Names for Ions and Radicals; Crystalline Phases of Variable Composition; Acids; Salts and Salt-like Compounds; Coordination Compounds and Polymorphism.

The rules are set out clearly and concisely. Naturally there are several interesting innovations proposed, some of which will be found hard to swallow by the present generation of inorganic chemists: e.g. the use of the term 'wolframate' in place of 'tungstate' and, harder still, 'wolframophosphate' in place of 'phosphotungstate'. The more logical term 'actinium series' is applied to elements 89 (Ac) to 103 and the term 'actinide' is reserved for those elements in which the 5*f* shell is being filled: similarly the name 'lanthanum series' is applied to elements 57 to 71 inclusive and the name 'lanthanide series' is used for elements 58 to 71.

However, we are not too rigidly bound by the new rules in the case of some long-established trivial names: we are still allowed 'sodium sulphate' in place of 'sodium tetraoxosulphate' and we are fortunate that in the great majority of rules logic has not been extended too far into pedantry. Some of the minor changes proposed seem a little illogical: e.g. the term 'nitr*ate* acidium ion' is to be used in place of the familiar 'nitr*ic* acidium' ion. An interesting innovation is the use of the term 'berthollide' for a non-stoichiometric compound. In the section on Salts and Salt-like Compounds useful recommendations are made to rid inorganic chemistry of some of its misleading names: e.g. calcium titanate becomes calcium titanium oxide. Logical rules for coordination compounds are put forward which can be extended to include other well-known compounds thus reducing the diversity of names in this field.

It is a feature of this book that the Commission has not been too pedantic in its recommendations and unequivocal terms in common usage are generally retained (there is not much doubt which of the following terms an inorganic chemist would prefer: calcium chloride-6-water and calcium chloride hexahydrate; the latter is permitted in the rules).

This book will clearly have a considerable impact on the language of inorganic chemistry and is a 'must' for practising inorganic chemists. It is clearly printed and conforms to the usual high standard of the publishers.

R. H. PRINCE

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Infra-red Spectra of Coal and Some Coal Derivatives

IF WE understand D. O. ALFORD[1] correctly, he wishes to suggest that the benzene extracts of Coals Nos. 2 and 3—infra-red spectra of which are reproduced in *Figure 2* of our paper[2]—are heavily contaminated with extraneous material. He agrees with our general assignment, by which the extracts are labelled as largely composed of aromatic esters, but considers that we have been misled by spurious introduction of butyl phthalyl butyl glycolate (or, alternatively, of dibutyl phthalate) into the extracts. The former substance (or a material closely similar to it) is, according to Alford, extracted when benzene is allowed to act on Tygon plastic tubing.

May we reiterate that the conditions under which we carried out the extractions make it exceedingly improbable that contamination with Alford's alternatives has occurred, and may we note also that the spectrum of Tygon benzene extract is *not*, as claimed by Alford, identical with the spectra of the benzene extracts of Coals Nos. 2 and 3. Several strong diagnostic bands (such as pronounced absorption at 1200 cm^{-1}) which occur in the Tygon extract spectrum are completely lacking in the spectra of the coal extracts; and there are also very significant differences in relative intensities. In short: in the face of the experimental evidence alone, there are indications of aromatic esters in the coal extract spectra, but none of the kind of contamination of which Alford speaks.

W. DEN HERTOG
N. BERKOWITZ

Research Council of Alberta,
Edmonton, Alberta

(*Received April 1959*)

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Action of Hydrogen Peroxide on the Acids obtained by the Controlled Oxidation of Bituminous Coal

IN OUR previous papers 1–14, the chemical structure of the more oxygen-resistant portion of bituminous coal was studied by investigating the structures of the acids obtained by controlled oxidation. This method of studying the structure of coal has the merit of employing the well established methods of organic chemistry. In this paper we wish to present the results of some further studies of these acids. It was thought that perhaps acids of simpler structure would result when the coal acids were oxidized by means of hydrogen peroxide. Inferences concerning the structures of the coal acids could then be drawn from the structures of these simpler acids. This general method has been used with success by V. T. BROOKS, G. J. LAWSON and S. G. WARD[5] and by G. J. LAWSON[6] in studying the structures of coal and humic acids.

The oxidation was carried out by heating aqueous solutions of coal acids and hydrogen peroxide for 24 hours at their boiling points using a reflux condenser to prevent excessive evaporation. The ratio of hydrogen peroxide to coal acids was varied and in addition to this, the hydrogen peroxide concentration was also varied by adding more or less water to the reaction mixture. In some of the experiments the amount of carbon dioxide obtained was determined by continuously sweeping the apparatus with a slow stream of nitrogen and absorbing the carbon dioxide in an Ascarite tube. The amounts of the volatile products formed were determined by mass spectrographic measurements made on the aqueous reaction mixture. In some experiments

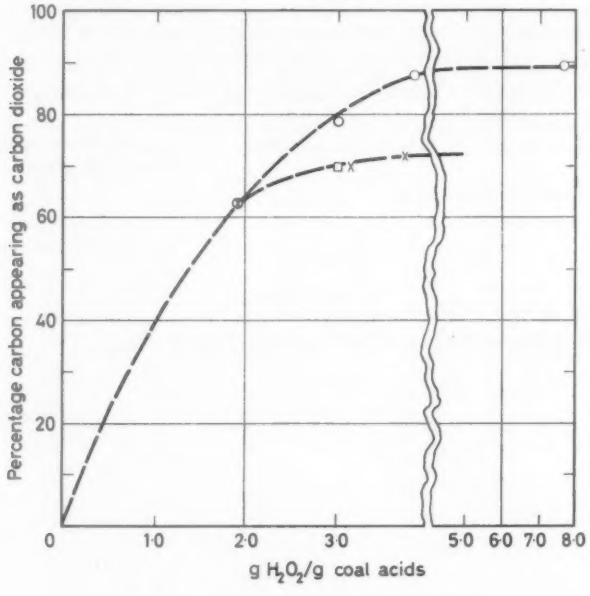

Figure 1. Yield of carbon as carbon dioxide

the reaction mixture was made basic, concentrated, and then re-acidified but this did not seem to increase the precision of the determinations.

Large amounts of carbon dioxide (*Figure 1*) were obtained but only small amounts of volatile organic acids (*Figures 2, 3* and *4*). Only propionic, acetic and formic acids could be identified among the products by means of mass spectrometry although traces of other masses were observed. Indirect evidence for the presence of oxalic acid was provided by the large amounts of carbon dioxide obtained in the mass spectra since oxalic acid is converted to carbon dioxide in the mass spectrometer. The action of hydrogen peroxide on aromatic acids seems to be quite complex. While part of the acetic and propionic acids in the oxidation products are undoubtedly produced from various aliphatic groups present on the aromatic coal acid structure, this is not entirely

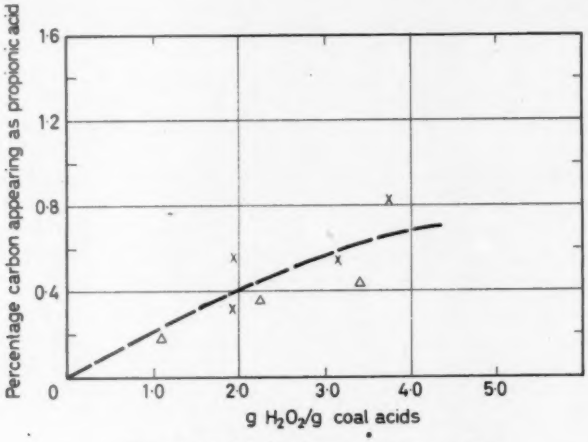

Figure 2. Yield of carbon as propionic acid

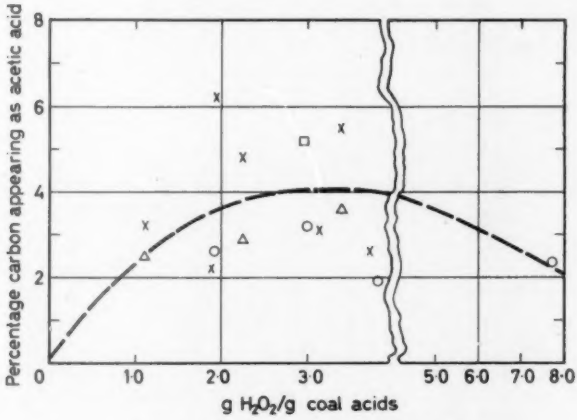

Figure 3. Yield of carbon as acetic acid

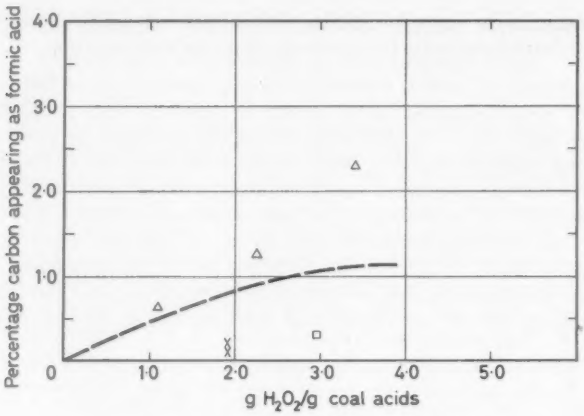

Figure 4. Yield of carbon as formic acid

the case. If these low molecular weight aliphatic acids originate entirely from aliphatic groups present on the aromatic acid structure, *ortho*- and *meta*-toluic acids would be expected to produce formic and acetic acids and phthalic acid would be expected to produce only formic acid. Actually, only acetic acid was obtained from the toluic acids and small amounts of all three low molecular weight aliphatic acids, i.e. formic, acetic and propionic, were obtained from phthalic acid.

In this oxidation, there did not appear to be any stable materials between the coal acids and the very low molecular weight acids. In one experiment the oxidation was stopped when only about half of the coal acids had been destroyed and the recovered methyl ethyl ketone-soluble acids appeared to be very similar to the starting material.

This method does not seem to be very useful as an aid to structure determination because only rather low molecular weight products can be obtained and the manner in which these products are obtained seems to be complex. The hydrogen peroxide oxidation appears to be similar to the alkaline-oxygen oxidation in that once the rather stable coal acid structure is destroyed, the fragments are rapidly degraded all the way to carbon dioxide and very low molecular weight acids. In both cases, products intermediate between the aromatic coal acids and acids such as propionic, acetic, and oxalic are not obtained.

R. S. MONTGOMERY
K. B. BOZER

The Dow Chemical Company,
Midland, Michigan

(Received March 1959)

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[5] BROOKS, V. T., LAWSON, G. J. and WARD, S. G. *Fuel, Lond.* 1956, **35**, 385
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PAPERS ACCEPTED FOR FUTURE PUBLICATION

The following papers have been accepted for publication in future issues of FUEL

THE DIFFUSION OF GASES THROUGH COAL. *P. G. Sevenster*

THE SEPARABILITY OF PYRITE PARTICLES IN SOME PULVERIZED COALS. *W. van Hees*

A MODIFICATION OF MOTT'S METHOD FOR THE DETERMINATION OF PYRITIC SULPHUR IN COAL. *W. van Hees and E. Early*

PYROLYSIS OF COAL I—THERMAL CRACKING OF PHENOLFORMALDEHYDE RESINS TAKEN AS COAL MODELS. *K. Ōuchi and H. Honda*

THE STRUCTURE OF COKE OVEN TAR. *E. W. Volkmann*

FURTHER STUDIES ON THE MECHANISM OF OXIDATION OF COAL. *B. K. Mazumdar, S. K. Chakrabartty, Mrs M. Saha, K. S. Anand and A. Lahiri*

CHEMICAL STRUCTURE AND PROPERTIES OF COAL XXIV—SOUND VELOCITY AND FRACTION OF AROMATIC CARBON. *D. W. van Krevelen, H. A. G. Chermin and J. Schuyer*

QUANTITATIVE DETERMINATION OF SOME POLYHYDRIC PHENOLS. *G. R. Boreham and J. A. P. Cunningham*

A NOTE ON THE RELATION OF SPECIFIC VOLUME OF COALS TO THEIR HYDROGEN AND OXYGEN CONTENTS. *S. Ergun, M. Mentser and H. C. Howard*

SOME OBSERVATIONS ON THE SPECIFIC SURFACE OF COALS. *S. J. Gregg and M. I. Pope*

A STUDY OF COAL BY MASS SPECTROMETRY. *H. W. Holden and J. C. Robb*

VERIFICATION OF THE H/C vs M_e/d DIAGRAM. *D. W. van Krevelen, J. A. Bigot and J. M. H. Fortuin*

THE DETERMINATION OF ACTIVE HYDROGEN IN COAL BY DEUTERIUM EXCHANGE. *L. Blom, L. Edelhausen and D. W. van Krevelen*

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